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ALKALI-ACTIVATED GEOPOLYMERS:
A LITERATURE REVIEW

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14. ABSTRACT

Information presented in this report is organized along specific issues such as the advantages and disadvantages of using geopolymer concrete for industrial applications, the benefits and risks associated with binder variables (alkaline concentration, pozzolan ratios, curing methodologies), mechanical variance resulting from differences in microstructural evolution and performance in harsh environments (extreme temperatures and chemical attack).

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1. INTRODUCTION

1.1. Background

Increasing emphasis on energy conservation and environmental protection has led to investigation of alternatives to customary building materials. Among the goals of these investigations are to reduce greenhouse gas emissions and minimize the energy required for material production. Currently, Portland cement is the leading material for industrial concrete demand worldwide, fulfilling a demand of over 1.5 billion tons annually. The production of Portland cement is energy-intensive and releases a significant volume of carbon dioxide (CO_2) to the atmosphere [1]. For each ton of Portland cement manufactured, it is estimated that one ton of CO_2 is released into the environment. The process involves very high temperatures (1400–1500 °C), the destruction of quarries to extract raw materials, and the emission of greenhouse gases such as CO_2 and NO_x [2]. The costs associated with these energy requirements are significant. Consequently, the need arose for further investigation into cementitious products with decreased environmental impacts and enhanced economic benefits.

Readily-available commercial by-products such as fly ash and blast furnace slag have been adopted to meet these demands. To this end, it was estimated that the amount of fly ash produced annually by the year 2010 will be about 780 million tons [3], providing a means to meet growing demand. The recycled use of this ash material in construction will alleviate the cost of disposal elsewhere and reduce the cost of concrete manufacture overall.

Figure 1. Fresh Geopolymer Binder Paste [4]

The term "geopolymer" is generically used to describe the amorphous to crystalline reaction products from the synthesis of alkali aluminosilicates with alkali hydroxide/alkali silicate solution. Geopolymeric gels and composites are also commonly referred to as low-temperature aluminosilicate glass, alkali-activated cement, geocement, alkali-bonded ceramic, inorganic polymer concrete, and hydroceramic [5]. A geopolymer paste as shown in Figure 1can be used to bind loose aggregates and other non-reacted materials together to form geopolymer concrete shown in Figure 2[6]. Geopolymer binders can provide comparable performance to traditional cementitious binders in a range of applications with the added advantage of significantly reduced greenhouse gas emissions [4].

Figure 2. Fresh Geopolymer Concrete [4]

1.2. Report Objective

The objective of this report was to evaluate geopolymer production methodologies and assess their potential as viable construction materials for industrial use. Specific topics detailed within the report include the following:

- Identification of factors influencing mechanical properties and durability
- Investigation of pozzolanic materials and their reactivity to various alkalines
- Curing methodologies and the variables affecting final strength characteristics
- Mineralogical and microstructural analysis of products
- Chemical and thermal resistance properties of geopolymer matrices
- Fiber reinforcement as a mechanical factor for toughness increase

1.3. Report Organization

This report details the recommended production and overall properties of alkali-activated, pozzolan-based geopolymer cements and concretes. It focuses upon the mineralogical and microstructural elements of the reaction products resulting from activation of commercially-produced fly ash, blast furnace slag, and other natural and readily-available pozzolans. The process of dissolution, polymerization and precipitation within the binder paste is discussed, and the resulting mechanics of the hardened material is evaluated. As a control, all observations of the geopolymer materials are related to the performance of known materials used currently in construction such as Portland cement concrete (PCC).

Information presented in this report is organized along specific issues such as the advantages and disadvantages of using geopolymer concrete for industrial applications, the benefits and risks associated with binder variables (alkaline concentration, pozzolan ratios, curing methodologies), mechanical variance resulting from differences in microstructural evolution and performance in harsh environments (extreme temperatures and chemical attack).

A comprehensive literature review of geopolymer cements is provided in the appendix of this report which contains short abstracts of all relevant reference material.

2. GEOPOLYMER THEORY

Geopolymerization is a geosynthesis–a reaction that chemically integrates minerals [3]. The exposure of aluminosilicate materials such as fly ash, blast furnace slag, or thermally activated substances to high-alkaline environments (hydroxides, silicates) gives rise to the formation of a geopolymer. Geopolymers are characterized by a two- to three-dimensional Si-O-Al structure [7]. These materials represent a new order of cementitious products able to provide ceramic and zeolitic properties not normally present in traditional cement materials.

2.1. Geopolymer Development

Geopolymer cements develop through a series of several distinct reaction processes from initial pozzolanic activation to final microstructure development. The benefits of using pozzolans as a matrix binder for agglomeration is that they tend to be economical, environmentally-friendly, more absorbent of liquids and produce a highly durable product [8]. The major processes are dissolution of the aluminosilicate species within a highly basic, alkaline environment, polymerization of the dissolved minerals into short-lived structural gel, precipitation of formed hydration products similar to natural zeolites and final hardening of the matrix by excess water exclusion and the growth of crystalline structures. Figure 3 illustrates the overall polymerization process in alkali-activated geopolymers.

2.1.1. Dissolution

Dissolution occurs immediately upon contact between the alkaline solution and the pozzolanic material and allows for ionic interface between species and the breaking of covalent bonds between silicon, aluminum and oxygen atoms. Similarly to PCC, this process generates rapid and intense heat (Fig. 4) and is directly proportional to the pH level of the activating solution. The rate of dissolution is relevant to the amount and composition of the ashes and the pH of the activating solution [9, 10].
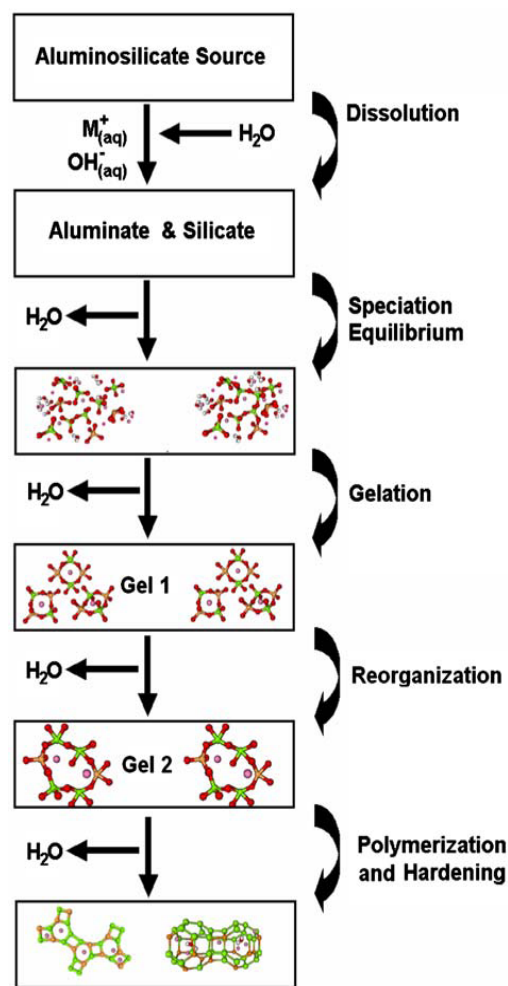
Figure 3. Geopolymer Development Model [5]
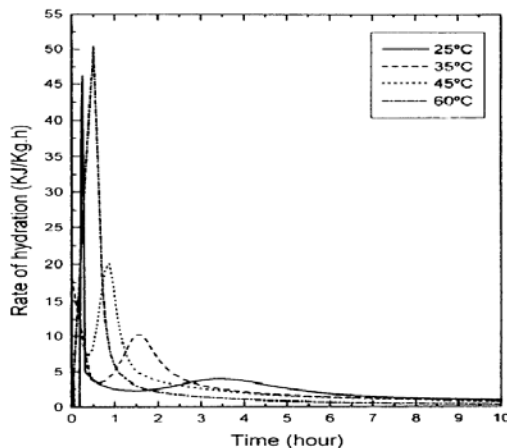
Figure 4. Rate of Slag-Based Geopolymer Hydration Heat vs. Time [11]

2.1.2. Polymerization

The polymerization process involves a substantially fast chemical reaction under alkaline conditions on Si-Al minerals, resulting in a three-dimensional polymeric chain and ring structure consisting of Si-O-Al-O bonds [6]. The formed gel product contains alkaline cations which compensate for the deficit charges associated with the aluminum-for-silicon substitution [10]. An intermediate, aluminum-rich phase is first formed which then gives way to a more stable, silicon-rich three-dimensional gel product of form Q^4(nAl), which is dependent upon curing conditions and activator type [9].

2.1.3. Growth

During this process, the slow growth of crystalline structures become evident as the nuclei of the polymerized gel reaches critical size. The matrix crystallinity is relative to the rate by which precipitation occurs: fast reactions between alkali and ash do not allow time for growth of a well-structured crystalline environment (representative of typical zeolites). Therefore, most hardened geopolymer cements are referred to as zeolitic precursors rather than actual zeolites. The final product of geopolymerization is an amorphous, semi-crystalline cementitious material.

2.2.   Hydration Reaction Characteristics

Within these process intervals, thermodynamic and kinetic parameters become vital to gel formation and reaction degree. Several factors directly influence the degree of reaction (α) observed in a mixed geopolymer paste and either enhance or detract from the polymerization process and subsequent phases that strictly define the formed cementitious properties of the hardened cement. The activation reaction rate as well as the chemical composition of the reaction products depends on several factors such as the particle size distribution and the mineral composition of the precursor fly ash [9]. A fly ash material used in a study (by Xie and Xi) contained a high fraction of reactive oxides which reacted significantly with a waterglass (Na_2SiO_3) activator, leading to a high strength within a short time and under relatively lower temperatures [12]. Likewise, alkaline activator types, concentration of activators, ratios of solids to liquids and curing temperatures and time are all relevant in the characterization of geopolymer

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cements and the mechanical properties attained. In practice, no matter which method is used, the selection of proper activators is the most important part of the technology [12].

2.3.   Alkaline Activators

The most common activators are hydroxides of sodium and potassium (NaOH and KOH). The highest observed mechanical strengths have resulted from the use KOH in varying concentrations. Since K^+ is more basic, it allows a higher rate of solubilized polymeric ionization and dissolution leading to a dense polycondensation reaction that provides greater overall network formation and an increase in the compressive strength of the matrix [3]. Conversely, a study by Arjunan *et al.* revealed that sodium hydroxide in low concentration was the most effective chemical activator for low calcium fly ash [13]. Regardless of type selected, however, higher concentrations of alkaline activators yield greater mechanical strength values. The pH level of the activating solution strongly influences the final cement performance. Khale and Chaudhary reported that the strength measured from samples of pH 14 were five times greater than samples formed from pastes of pH 12; and they concluded that a pH range of 13–14 was most suitable for the formation of geopolymers with higher mechanical strengths [3].

While the mechanical properties of alkali-activated cement products show satisfactory values, a primary concern of geopolymer production is the ability to attain proper curing without external heating. PCC products are capable of achieving full strength in ambient temperatures but may not perform well in harsh environments. One motivator for adopting geopolymer binder is its ability to resist sulfate and other chemical intrusions and maintain excellent thermal loading capacities. However, the question of curing in field applications is a relevant concern limiting the utility of geopolymer as a practical construction material.

The tests reported by Sumajouw *et al.* revealed that geopolymer concretes possess high compressive strength, undergo very little drying shrinkage and exhibit moderately low creep. Their data also indicate that geopolymer concretes possess excellent resistance to sulfate attack, resulting in a promising construction material for some harsh environments [1].

3. GEOPOLYMER BINDER CONSTITUENTS

3.1. Pozzolanic Materials

A pozzolan is defined as finely divided siliceous or aluminous and siliceous material that reacts chemically with slaked lime at ordinary temperature and in the presence of moisture to form strong, slow-hardening cement with two disadvantages: they are slower to set and can be intolerant to impurities such as clays, metal ions, sulfides, phosphates, etc. [8]. Materials rich in silicon (such as fly ash or slag) and materials rich in aluminum (kaolin clay) are the primary requirement for geopolymerization to occur [3].

3.1.1. Commercial Fly Ash

Most of the globally-available fly ash material is a low-calcium by-product obtained from the burning of anthracite and bituminous coal. It is considered one of the most important source materials for geopolymer cements [5, 3]. In general, fly ash is an acidic material containing acidic oxides such as Al_2O_3, SiO_2 and Fe_2O_3 which provide a potential for alkali reaction [12]. Most fly ashes from the combustion of coal are made up of an inhomogeneous mix of aluminosilicate and silica glasses plus small amounts of crystalline materials including mullite, quartz, hematite and magnetite [14]. This degree of inhomogeneity means that additional care is required to ensure an optimal mix design and consistent final product [5].
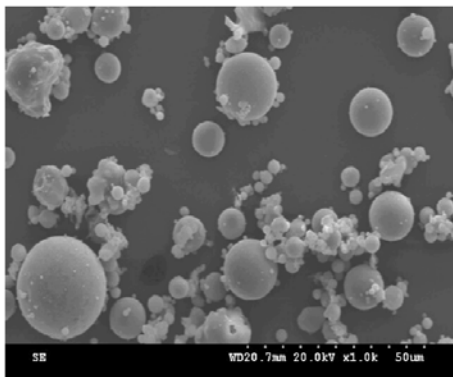
Figure 5. Microscopic Image of Raw Commercial Fly Ash [16]

Particle size distribution and particle fineness are the physical characteristics of fly ashes (shown in Figure 5) most strongly affecting their reactivity, whereas relative silica content is most influential from a chemical perspective [15]. The presence of highly reactive silica in the ash increases the formation potential of the aluminosilicate gel which provides mechanical strength to geopolymers. Aside from this point, the ability for a specific fly ash material to be alkaline-activated is driven by several other factors: the percentage of unburned material in the ash product act as inert particles causing an increase to the liquid/solid ratio and the content of its vitreous phase, these inert particles are all products of the original coal combustion method [15]. Fernandez-Jimenez et al. found that fly ashes with a highly reactive SiO_2 and Al_2O_3 content and Si/Al ratios below 2.0 perform best under alkaline activation [10]. Table 3 categorizes potential geopolymer uses by their inherent Si/Al ratio value.

The final reaction product of alkali-activated fly ash is an amorphous to semi-crystalline structure similar to a zeolite precursor. The activation process and degree of reaction within the geopolymer paste is directly related to the glassy content of the ash material [15]. The key to a fly ash-based geopolymer product with optimum binding properties was stated by Ferndandez-Jimenez to be derived from using a fly ash material with the following properties: less than five percent of unburned material; less than 10 percent Fe_2O_3; a low content of CaO; 40–50 percent relative silica; 80–90 percent of particles with diameter equal to of less than 45 µm; and a high vitreous phase [15].

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Table 1. Applications of Geopolymer Materials as Related to Atomic Si/Al Ratios [4]

Si:Al Ratio	Applications
1	• Bricks • Ceramics • Fire Protection
2	• Low CO_2 Cements and Concretes • Radioactive and Toxic Waste Encapsulation
3	• Fire Protection Fiberglass Composites • Foundry Equipment • Heat Resistant Composites, 200°C to 1000°C • Tooling for Aeronautics Titanium Process
>3	• Sealants for Industry, 200°C to 600°C • Tooling for Aeronautics SPF Aluminum
20-35	• Fire Resistant and Heat Resistant Fiber Composites

The aluminum content of a fly ash material is critical to the hardening properties of a geopolymer binder. In the presence of alkali aluminosilicate slurries, the aluminum content is believed to be the chemical trigger for irreversible cement hardening [5]. The dissolution of solid Al_2O_3 regions by the activating solution controls the rate, stoichiometry, and extent of solution phase reactions and is dependent upon several variables including pH level, binder temperature, the Si/Al ratio and alkali concentration [5]. For this reason, the composition and mineralogy of raw pozzolans is critical in the formulation of alkali-activated geopolymer materials. The increase in performance relative to the Si/Al ratio can be summarized by Figure 6 and Figure 7 illustrating increasing densities with increasing Si/Al ratios.
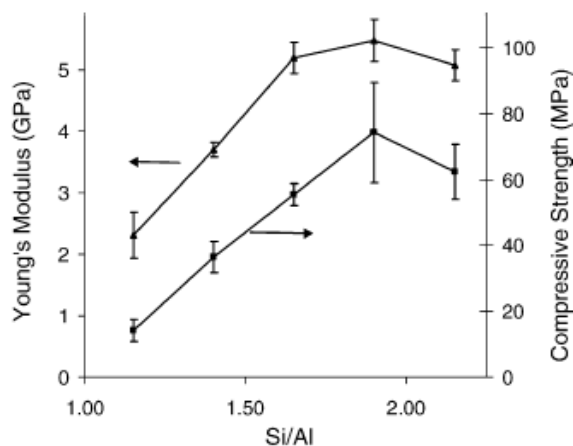
Figure 6. Mechanical Performance of Geopolymers Relative to Si/Al Ratio [17]
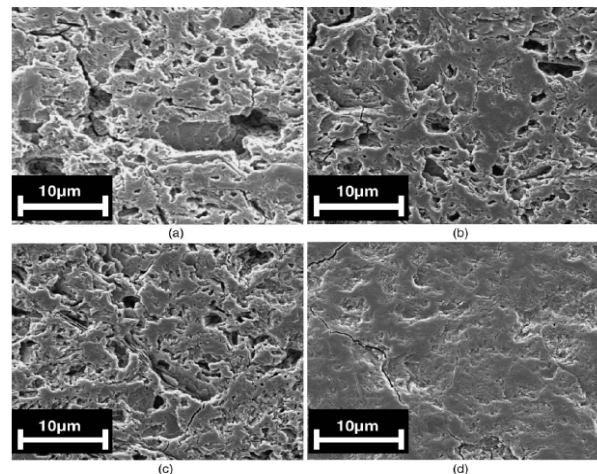
Figure 7. SEM Micrographs of Geopolymers with Si/Al= (a) 1.45, (b) 1.50, (c) 1.55, (d) 1.60 [17]

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3.1.2. Commercial Blast Furnace Slag

Ground granulated blast furnace slag (GGBFS) is another industrial by-product resulting from rapid water cooling of molten steel. It is known to have advantageous properties for the concrete industry as it is relatively inexpensive to obtain, highly resistant to chemical attack and maintains excellent thermal properties. Major components of the slag product include SiO_2, CaO, MgO and Al_2O_3—commonly found in commercial silicate glasses. Its relative reactivity potential derives from chemical composition, glass phase content, surface morphology and particle size distribution [18]. Typical slag products are ground, granulated and mixed with 3.5–5.5 percent (by mass) sodium hydroxide or waterglass. Alkali-activation yields a low-basic, highly amorphous calcium silicate hydrate (C-S-H) gel product possessing high aluminum content [19]. This product is referred to by some as alkali-activated slag (AAS).

Chemical shrinkage and porosity volumes in saturated GGBFS pastes are significantly higher than in Portland cement pastes and is a legitimate concern during setting [19]. Drying shrinkage is a direct result of hydration heat and increases with increased n modulus and dosage of waterglass activators [20]. Alternatively, the increase in alkaline concentration in the paste mix increases the degree of hydration reaction [19] and reduces pore volumes improving microstructural properties of the C-S-H product. While shrinkage in AAS pastes is more relevant than in Portland cement products, it maintains a much higher ultimate strength by comparison and remains a viable material for commercial use.

3.1.3. Calcined Metakaolin

Metakaolin is a dehydroxylated pozzolanic product derived from the high-temperature firing of raw kaolin. Kaolin, or kaolinite [$Al_2Si_2O_5(OH)_4$], is a clay mineral containing high amounts of layered tetrahedral silicon atoms connected via oxygen to octrahedral aluminum atoms. It is commonly used in the manufacture of porcelain.

Kaolin contains hydroxyl ions that are strongly bonded to the aluminosilicate framework and can only be altered by temperatures above 550 °C, thus rearranging the atomic structure to form a partly ordered system with great reaction potential to alkaline solutions [21]. The optimum temperature and duration for converting kaolin into metakaolin is 600 °C for two hours [22]. The resulting metakaolin substance is highly reactive and serves as an excellent addition to fly ash for use as a binder in geopolymer cement. Replacement of traditional fly ash material with metakaolin by up to 30 percent (by mass) yielded compressive strength values of 30–50 MPa for mortar specimens tested by Chareerat *et al.* [22]. Whereas fly ash material can contain contaminants which affect the final product, metakaolin-based geopolymers can be manufactured consistently with a high level of predictability in hardened characteristics [5]. Figure 8 displays compressive strengths and porosities for both metakaolin geopolymers and metakaolin/fly ash mixtures.
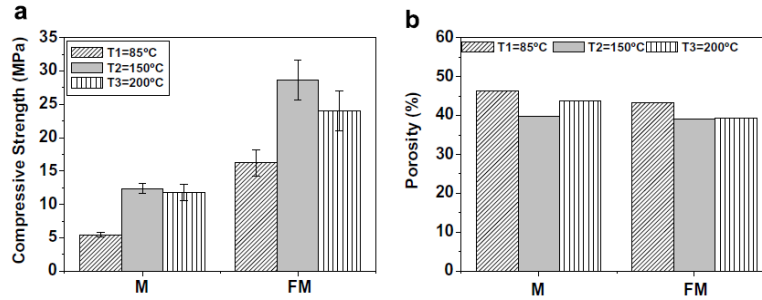
Figure 8. Mechanical Strength and Porosity of Metakaolin Geopolymers [21]

3.1.4. Blaine Fineness

The Blaine Fineness of a pozzolanic material is the relative measure of particle size ratio. Smaller (or fine) particles are more reactive in solution partially because they have a greater surface area for chemical contact. Higher fineness values produce cements with lower porosity and higher mechanical strengths. The optimum Blaine fineness for blast furnace slag ranges between 4000 and 5500 cm^2/g (depending upon slag type); values above 5500 have little effect on mechanical strength for slag materials [23]. However, research by Pacheco-Torgal reveals that while higher fineness for slag materials results in greater reactivity, it also demands additional hydration, leading to an increase in porosity and lower mechanical strength [19]. Figure 9 shows the compressive strength values for two separate fly ash samples; samples represented in graph (a) were mixed and tested as received from the supplier, while all particulates greater than 45 microns in diameter have been removed from the ash sample shown in graph (b). This data supports the theory which projects greater performance from ash samples of finer proportion.
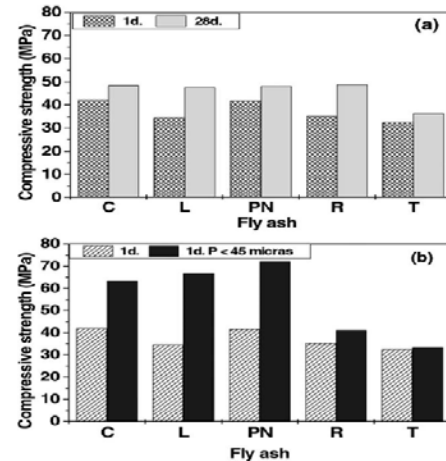
Figure 9. Compressive Strengths of Fly Ash Mortars (20 Hrs, 85 °C); (a) 1 and 28 Days Raw Material, (b) 1 Day, Material Fineness Less Than 45 Micrometers [15]

3.2. Alkaline Activators

Activation of the selected pozzolanic material is the most significant factor in producing a mechanically-sound cementitious material via the geopolymerization process. The activators prompt the precipitation and crystallization of the siliceous and aluminous species present in the solution. OH⁻ acts as a catalyst for reactivity, and the metal cation serves to form a structural element and balance the negative framework carried by the tetrahedral aluminum [5]. The initial mechanism of reaction is driven by the ability of the alkaline solution to dissolve the pozzolanic material and release reactive silicon and aluminum into solution.

When fly ash or other pozzolans are mixed with alkaline solutions, their vitreous component is quickly dissolved. There is not sufficient time or space for the resulting gel to grow into a well-crystallized structure. As a result a micro-crystalline, amorphous or semi-amorphous structure is

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formed [3]. The following is a classification of various groups of activating agents where M represents an alkali ion (Pacheco-Torgal *et al.*):

- Alkalis, MOH
- Weak acid salts, M_2CO_3, M_2SO_3, M_3PO_4, MF
- Silicates, $M_2O * nSiO_3$
- Aluminates, $M_2O * nAlO_3$
- Aluminosilicates, $M_2O * nAl_2SO_3 * (2\text{-}6)SiO_2$
- Strong Salt Acids, M_2SO_4

While common activators include NaOH, Na_2SO_4, waterglass, Na_2CO_3, K_2CO_3, KOH, K_2SO_4 and cement clinker [3], the most utilized alkaline activators are a mixture of sodium or potassium hydroxides (NaOH, KOH) and sodium waterglass ($nSiO_2Na_2O$) or potassium waterglass ($nSiO_2K_2O$) [23].

3.2.1. Sodium Hydroxide (NaOH)

NaOH is also commonly used as an alkaline activator in geopolymer production. While it does not maintain the level of activation as a K^+ ion, sodium cations are smaller than potassium cations and can migrate throughout the paste network with much less effort promoting better zeolitization [5]. Furthermore, it bears a high charge density which promotes additional zeolitic formation energy.

The concentration and molarity of this activating solution determines the resulting paste properties. While high NaOH additions accelerate chemical dissolution, it depresses ettringite and CH (carbon-hydrogen) formation during binder formation [3]. Furthermore, higher concentrations of NaOH promote higher strengths at early stages of reaction, but the strength of aged materials were compromised due to excessive OH^- in solution causing undesirable morphology and non-uniformity of the final products [3]. It is found that geopolymers activated with sodium hydroxide develop greater crystallinity thus improving stability in aggressive environments of sulfates and acids [25].

Additionally, the use of sodium hydroxide as an activator buffers the pH of pore fluids, regulates hydration activity and directly affects the formation of the main C-S-H product in geopolymer pastes [18]. There is a linear relationship between NaOH concentration and the heat generation; however, there exists an inverse relationship between concentration and the time at which maximum hydration heat occurs [18].

3.2.2. Potassium Hydroxide (KOH)

KOH has been found to produce high compressive strengths and improved porosity in geopolymer cements. Since K^+ is more basic than other activating ions, it possesses a greater potential for polymeric ionization in solution resulting in high reactivity of the prime pozzolan, a denser final product and a matrix formation capable of achieving increased compressive strength values [3]. However, KOH concentrations above 10 M have been shown to decrease strength due to excessive K^+ ions in solution and Si/Al leaching of KOH based cements occurred more than those derived from NaOH activation [3]. While KOH is reasoned to provide a greater extent of dissolution due to its higher level of alkalinity, NaOH actually possesses a greater capacity to liberate silicate and aluminate monomers [5].

3.2.3. Sodium Silicate (Na_2SO_3)

Sodium (or potassium) silicates are manufactured by fusing sand (SiO_2) with sodium or potassium carbonate (Na_2CO_3 or K_2CO_3) at temperatures in excess of 1100 °C and dissolving the product with high pressure steam into a semi-viscous liquid referred to as waterglass [8]. Waterglass is rarely used as an independent activating unit, because it does not possess enough activation potential to initiate pozzolanic reaction alone. Rather, it is commonly mixed with NaOH or KOH as a fortifying agent to enhance alkalinity and increase overall specimen strength. The most common alkaline liquid used in geopolymerization is a combination of sodium hydroxide or potassium hydroxide and sodium silicate or potassium silicate [7].

Sodium silicate solution is commercially available in different grades [6], but it should be noted that powdered waterglass leads to lower performance compared to the liquid form [23]. For best results, a silicate solution with a SiO_2 to Na_2O ratio (by mass) of 2.0 mixed with an 8–16 M activator 24 hours prior to use is recommended [6].

The most important property of this product is its mass ratio of SiO_2 to Na_2O, which is commercially available in the range of 1.5 to 3.2 (with 3.2 being the best suited for geopolymerization) [8]. Soluble silicates reduce alkali saturation in pore solution and promote greater interparticle bonding with both geopolymer binders and the included aggregate material [26]. Testing has revealed that activating solutions containing little or no soluble silicates produced significantly weaker compressive strengths of mortars and concretes than those activated with high doses of soluble silicates [26]. As well, the presence of such silicate material improves interfacial bonding between rock aggregates and geopolymer mortars [26]. On the contrary, additional research shows that under increasing temperatures, specimens containing waterglass decrease in strength while those containing only a base activator (NaOH, KOH) produce higher strengths.

Additional research is still required to accurately determine the specific effects produced through the addition of waterglass into geopolymer binder solutions.

3.3.   Binder Constituent Proportioning

Geopolymer binder properties are highly dependent upon the type, ratios and concentrations of mixing constituents. Each constituent and the variables associated with that constituent play a significant role in determining the characteristics of the final product.

3.3.1. Activator Concentration

The alkaline activator concentration is the most critical factor for successful geopolymer formation and the evolution of high compressive strength. Regardless of activator type, an increase of concentration increases the reaction rate and degree leading to a less porous and stronger cement material. The addition of activators and increase in concentration results in an increase in volume of smaller pores and lower total porosity for the fly ash-based systems, thus increasing early strength of the mortars samples [18].

The influence of activator concentration increases with time. The nominal molarity for fly ash and GGBFS mixes range from 2–10 M, but higher strengths are obtained when the concentration approaches the maximum range [27]. While it is generally accepted that a higher concentration

will result in higher strength capabilities, there seems to be an optimum limit for each activator type, such that crossing this limit results in the reverse affect. Specimens created using a 10 M KOH solution showed the highest compressive strength of 60 MPa, but the strength decreased as the KOH concentration was raised to 15 M [3]. It is believed that the mixture exceeded its saturation point and the unreacted K^+ ions became deterrent to strength gain rather than a benefit. Consequently, a higher alkaline concentration increases set time and delays polymer formations since excessive ion presence limits their mobility and potential to interact with available reactive species. For this reason, the concentration must be addressed clearly in a geopolymer mix design.

3.3.2. Pozzolan/Activator Ratio

The ratio of pozzolanic material (fly ash, blast furnace slag, calcined clays) to a selected activator affects several critical properties of the geopolymer basis. Overall strength is greatly affected by this variable. The alkaline liquid-to-fly ash ratio (by mass) is recommended to be maintained in the range of 0.30 to 0.45 [6]. Higher compressive strengths were obtained when experimentation was conducted using 5 M activator concentrations and a liquid-to-fly ash ratio of 0.4 [16].

The fly ash-to-activator ratio appeared to be the most critical parameter regarding general strength and fire resistance of the geopolymer paste [28].
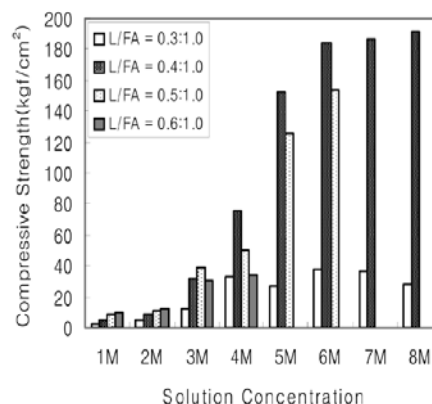
Figure 10. Effect of Liquid Activator Concentration-to-Fly Ash Ratio on Compressive Strength [16]

3.3.3. Sodium Silicate / Hydroxide Activator Ratio

The addition of sodium silicates to the mix design increases mechanical properties beyond the ability of a hydroxide activator alone. However, care must be taken to regulate the ratio between each substance. Laboratory experience suggests that the ratio of sodium silicate-to-sodium hydroxide solution (by mass) be set to an approximate value of 2.5 [6].

3.3.4. SiO$_2$ / Na$_2$O Ratio (M$_s$ Modulus)

The SiO$_2$ / Na$_2$O ratio is a highly important parameter in geopolymer design. It is well known that variations in the SiO$_2$ / Na$_2$O ratio significantly modifies the degree of polymerization of the dissolved species in the alkaline/silicate solution, thus determining the mechanics and overall properties of the synthesized gel product [5]. Higher percentages of soluble silica in geopolymer systems retards dissolution of the ash material due to increased saturation of the ionic silica species and promotes the precipitation of larger molecular species, resulting in a stronger gel with an enhanced density [29]. At intervals of short cure times, an increase in soluble silica favored the development of high mechanical strength, while lower silica content produces the highest strength values at longer cure times [29]. The presence of soluble silica directly affects the reaction kinetics, the rate of crystallization, and promotes a Si-rich gel formation which is responsible for material strength development. A ratio of 2.0 for commercially available SiO$_2$ to Na$_2$O (by mass) is recommended [6]. Figure 11 illustrates the inverse relationship between Na$_2$O and SiO$_2$ on compressive strength characteristics; strength increases with an increased presence of SiO$_2$.
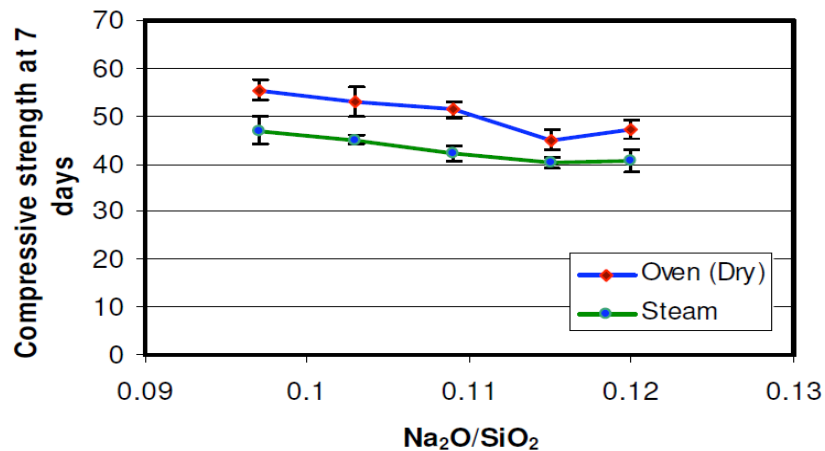
Figure 11. Effect of Molar Na$_2$O/SiO$_2$ Ratio on Compressive Strength [29]

3.3.5. pH Level

The most significant factor affecting compressive strength in geopolymers is pH, with a range of 13–14 being the most suitable for development of good mechanical strength [3]. An increase of the alkaline activator concentration directly raises the pH and consequently enhances the degree of reaction. An increased level of pozzolanic reactivity yields a denser and stronger matrix due to less void space and unreacted particles. The pH also affects the viscosity of the geopolymer mixture: added pH reduces viscosity and the paste becomes more workable, while a lower pH level causes the paste to remain viscous and stiff [3]. With a higher pH, a predominance of smaller chain oligomers and monomeric silicate available to react with soluble aluminum was observed, while lower pH levels produced lower monomer concentration [3].

4. GEOPOLYMER CONCRETE PRODUCTION

This section describes the recommended technology for designing, mixing, and curing geopolymer mortars and concretes. Every aspect of the design must be thoroughly investigated and engineered in order to avoid unwanted results and ensure optimum performance for each given service scenario.

4.1. Aggregates

Aggregates in geopolymer concrete serve the same purpose as in Portland cement-based materials, but care must be taken to avoid potential issues from possible aluminosilicate reactivity (ASR) with the alkaline activating solution. Mineral composition including opaline, cryptocrystalline silica, chalcedony and microcrystalline quartz are susceptible to ASR attack which could ultimately lead to aggregate dissolution [31]. Furthermore, the reactions can form crystalline structures of expansive nature, causing internal stress cracking and material spalling. The replacement of calcium-rich Portland cement with pozzolans such as fly ash and blast furnace slag have greatly reduced the potential for ASR to exist; however, this issue must be addressed prior to selection of an applicable aggregate material.
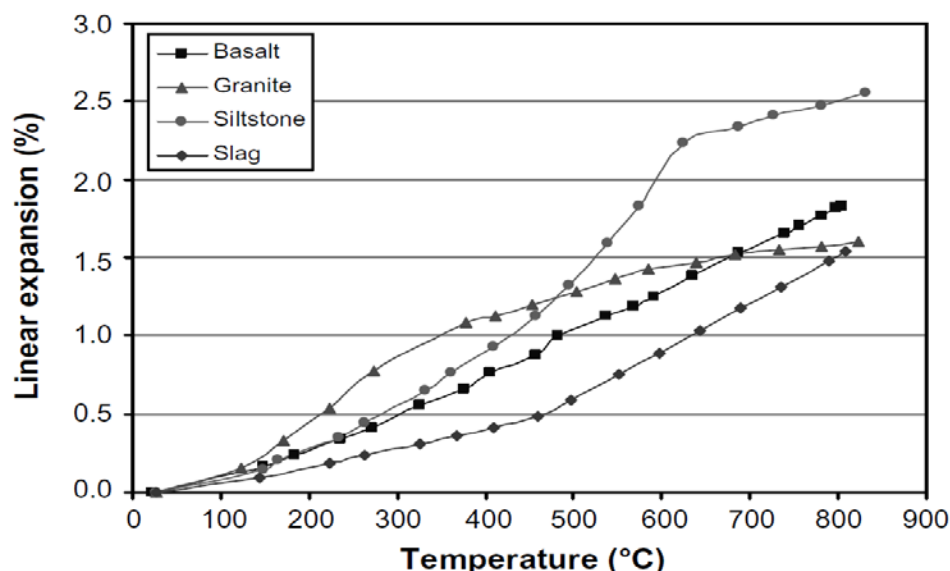
Figure 12. Thermal Expansion Characteristics of Coarse Aggregates Under Extreme Thermal Loading [31]

The recommended mass of combined aggregates for geopolymer mortars and concretes is 75-80 percent of the total geopolymer concrete mass [6]. The fineness modulus of combined aggregate material is best set to 4.5 or 5.0 to allow for maximum interaction and bonding with the geopolymer binder paste solution [6]. The aggregate material is used primarily for filler material to reduce the amount of binder required for production; no added benefit from aggregate inclusion is observed. The geochemical nature of the coarse aggregates (basalt or siltstone) appear to have little effect on the compressive strength of geopolymer concretes; however, basalt yields a slightly stronger interfacial bonding strength than siltstone rock [26].

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The coarse and fine aggregates in a geopolymer concrete mixtures are assumed to be saturated surface dry (SSD) to prevent either water absorption or addition to the mixture. In reality, this may not be the case and additional water from the aggregate material will inadvertently be introduced to the system. For this reason, it is recommended to allow for slight compensation in the water-to-solids ratio within the geopolymer mix design.

The interfacial bonding between the binder paste and aggregate mix is highly dependent upon the alkaline activator concentration. When the activating solution was low in alkalis and/or soluble silicate, the interfacial bonding strengths between the rock and the geopolymer mortars were also low [26]. While the potential for interfacial bonding is high with the proper alkalinity, additional research shows that thermal loading of geopolymers containing coarse aggregate can be detrimental to the concrete system. The strength of the fly ash-based geopolymer declined with the inclusion of aggregate materials, possibly due to the differential in thermal expansion between the paste and aggregate masses [28]. It is believed that the geopolymer matrix experiences thermally induced contraction, while the aggregates expand upon extreme loading. Additional research is required to successfully identify this phenomenon.

4.2. Mixture Proportioning

Geopolymer components play an important role in determining final product characteristics. The mechanics of hardened geopolymer mortars and concretes are directly related to factors such as pozzolan composition, activator type and concentration, aggregate size and ratios of added liquids (water, plasticizers). Furthermore, the proportion of each component as related to the whole is critical in the successful development of strength-supporting structures within the geopolymer matrix.

Fly ash composition is generally measured and evaluated by the percentage of existing elements present in the by-product material (Table 2), while other proportioned variables are typically by relative mass, molarity and fluid volume. Table 3 outlines a typical proportion used for a geopolymer mix design. High levels of silicon and aluminum are critical for product development; therefore, the Si/Al ratio in the initial pozzolan bear great significance to the strength potential of a given geopolymer specimen.

Table 2. Typical Fly Ash Composition (%) [32]

SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	LOI
45.32	20.92	10.7	7.6	1.8	0.2

Table 3. Typical Geopolymer Mixture Proportions [32]

Mix ID	W/B	FA	Agg.	S	W	Na$_2$O : SiO$_2$	NaOH
					kg/m^3		
1	0.40	514	1056	700	95	127	55(15 M)
2	0.42	514	1056	700	119	79	79(15 M)
3	0.41	514	1056	700	119	79	79(20 M)
4	0.47	475	1056	700	79	158	79(15 M)
5	0.46	475	1056	700	79	158	79(20 M)
6	0.48	475	1056	700	79	119	119(15 M)
7	0.46	475	1056	700	79	119	119(20 M)

w/b = water to binder ratio, FA = fly ash, Agg. = Aggregate, S= sand, W= water

Chemical ratios are also vital in geopolymer creation. Much research has been completed to determine the direct relation between chemical ratios and final strength values, but definitive optimal ratios have yet to be clearly established. Table 4 lists typical ratios for various chemical additives in several geopolymer mixtures.

Table 4. Typical Chemical Ratios of Activated Fly Ash Paste [32]

MIX ID.	Chemical Ratios			
	Na$_2$O/SiO$_2$	SiO$_2$/Al$_2$O$_3$	H$_2$O/Na$_2$O	Na$_2$O/Al$_2$O$_3$
MIX 1	0.115	4.276	22.135	0.492
MIX 2	0.139	4.051	20.249	0.563
MIX 3	0.160	4.051	17.173	0.647
MIX 4	0.162	4.488	17.648	0.727
MIX 5	0.182	4.488	15.304	0.818
MIX 6	0.213	4.285	14.080	0.914
MIX 7	0.245	4.285	11.804	1.051

In order to achieve high strength and durability, based on the zeolite chemistry, the use of certain molar ratios is recommended for the alkaline activator: SiO$_2$/Na$_2$O = 1.85; for the metakaolin: SiO$_2$/Al$_2$O$_3$ (3.5–4.5), Na$_2$O/SiO$_2$ (0.2–0.48), Na$_2$O/Al$_2$O$_3$ (0.8–1.6); between the activator and the metakaolin: H$_2$O/Na$_2$O(10–25) [43]. Tables 5 and 6 represent proportionality values for concrete and mortar mixture designs by Wallah and Rangan [46].

Table 5. Typical Geopolymer Concrete of Aggregates and Liquids [4]

Materials		Mass (kg/m^3)	
		Mixture-1	Mixture-2
Coarse aggregates:	20 mm	277	277
	14 mm	370	370
	7 mm	647	647
Fine sand		554	554
Fly ash (low-calcium ASTM Class F)		408	408
Sodium silicate solution(SiO$_2$/Na$_2$O=2)		103	103
Sodium hydroxide solution		41 (8M)	41 (14M)
Super Plasticiser		6	6
Extra water		0	22.5

Table 6. Typical Geopolymer Mortar Mix [4]

Materials	Mass (kg/m^3)
Fine sand	1052
Fly ash (low-calcium ASTM Class F)	774
Sodium silicate solution (SiO$_2$/Na$_2$O=2)	196
Sodium hydroxide solution (8M)	78
Super Plasticiser	12

While each component used to formulate the geopolymer bears significance to the final product, it has been determined that the optimum composition resulted from the following chemical ratios: Na$_2$O/SiO$_2$ = 0.25; H$_2$O/Na$_2$O = 10; and SiO$_2$/Al$_2$O$_3$ = 3.3 [34]. Furthermore, water content was recognized as an important factor to the success of the geopolymer, as testing with H$_2$O/Na$_2$O molar ratios equal to 25 produced extremely low mechanical results [34]. It must be stated, however, that while the proportioned values given by specific research publications are deemed as optimum, further investigation is required to fully understand the intrinsic behavior of each component as it relates to the mechanics of the final geopolymer product.

4.3.   Consolidation Techniques

The inherent viscosity of fresh geopolymer pastes causes excessive air entrainment during the mixing process. Trapped bubbles have difficulty escaping the thick matrix without mechanical aid. Vibratory plates and ultrasonic technologies are proven methods for helping to reduce air entrainment and improve the hardened porosity.

4.3.1. Mechanical Vibration

Mechanical vibration of the fresh geopolymer paste material substantially reduces trapped air pockets and improves the porosity of the final product. The aluminosilicate gel is highly viscous and mixing agitation can easily encapsulate air into the matrix. Vibration of the formed molds serves to reduce this potential and greatly improves the overall strength of the hardened geopolymer concrete.

4.3.2. Ultrasonication

The technique of ultrasonication throughout the fresh paste material was developed to reduce porosity and increase the compressive strength of geopolymer cements. Initial ultrasonication enhanced dissolution, thus promoting the release of additional aluminum and silicon into the gel phase and strengthening the particle surface bonds [35]. It also improved the formation of semi-crystalline to crystalline phases in the hardened cements products. The accelerated dissolution of the Al-Si source materials served to improve the compressive strength and develop thermal stability properties not observed in specimens absent from ultrasonication [35].

Table 7. Compressive Strength of Geopolymers Synthesized with Ultrasonication [35]

Condition		Compressive strength (MPa)
60 g metakaolinite, 160 g sand 0.5 M Na_2SiO_3, 10 M NaOH	Without ultrasonication	7.6
	Ultrasonication time (min)	
	4	10.0
	8	12.5
	14	15.0
	20	15.5
60 g metakaolinite, 160 g sand 2.5 M K_2SiO_3, 8 M KOH	Without ultrasonication	15.8
	Ultrasonication time (min)	
	1	22.0
	3	24.3
	5	24.5
225 g fly ash, 25 g metakaolinite 2.5 M K_2SiO_3, 8 M KOH	Without ultrasonication	11.8
	Ultrasonication time (min)	
	1	13.4
	3	18.5
	5	19.1
200 g fly ash, 50 g metakaolinite 2.5 M Na_2SiO_3, 8 M KOH	Without ultrasonication	14.8
	3 min ultrasonication	23.2

4.4. Curing Methodologies

4.4.1. Ambient Temperature Cure

A challenge for successful geopolymer concrete production is obtaining proper mechanics at ambient temperatures. Similar to Portland cement, the geopolymer reaction is more easily achieved with the addition of an external heat source to promote alkaline reactivity of the pozzolanic material. There is a challenge in synthesizing fly ash based geopolymers at ambient temperatures, as others have found that geopolymers did not set at 23 °C [36]. While it may be feasible to expose test specimens to elevated temperatures in a laboratory, a full scale pavement project would be difficult to efficiently heat during cure.

Research has been completed to investigate geopolymer designs with the potential to successfully harden under room temperature environments, yet little understanding has been gained regarding methods of large-scale ambient geopolymer cure. However, it was stated by Rangan (2008) that heat-curing temperatures can be as low as 30 °C, which

Figure 13. Compressive Strength of Specimens Cured at Ambient Temperatures [4]

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would be attainable in tropical climate conditions [6]. Figure 13 represents ambient-cure research performed by Wallah and Rangan that shows achieved compressive strength values beyond 50 MPa for specimens cured at temperatures ranging from 8 to 25 °C and relative humidity of 40–60 percent. While full-scale ambient cure presents logistical difficulties, an option for field implementation would be thermal loading of pre-cast concrete sections prior to field delivery. This method could be a viable solution until a deeper understanding of ambient cured geopolymer is properly developed.

4.4.2. Elevated Temperature Cure

As with traditional Portland cements, geopolymers respond better to heated curing methods. Research work has demonstrated that time and temperature greatly affect the mechanical development of geopolymer binders; however, a temperature threshold exists, beyond which the strength gain rate is extremely slow [5]. Temperatures in the range of 50–80 °C are widely accepted values used for successful geopolymer hydration. Both curing temperature and curing time directly influence final compressive strength values of geopolymer specimens.

Elevated temperature curing can be achieved through the use of steam or dry-heat methodologies, but test data shows that dry-curing yields a compressive strength increase of 15 percent over the steam curing methods [6].

While it has been noted that an increase of reaction time and temperature positively affect geopolymerization, similar research shows that these factors are only an enhancement to mechanics at an early age. As reaction time increases at later ages, the curing temperature increment has a negative effect, provoking a decrease in final strength values [38]. The basis for explanation lies within the initial heavy formation of the reaction product and a subsequent densification of material immediately upon alkaline introduction. The reaction product becomes exponentially less over time and increased temperatures only serve to degrade previously created aluminosilicate gels within the matrix, thus weakening the overall structure.

4.4.3. Post-Cure Thermal Loading

Since geopolymers inherently possess high levels of thermal resistance, research has been conducted to determine the mechanical and micro-logical effects of extreme temperature exposure of various geopolymer cements and mortars. Specimens were subjected to temperatures of up to 1200 °C and analyzed for resulting compressive and bending strength, thermal conductivity, specific heat capacity and porosity. SEM analysis of geopolymers matrices (Fig.14) reveal micrological characteristics of specimens thermally loaded at varying temperatures.
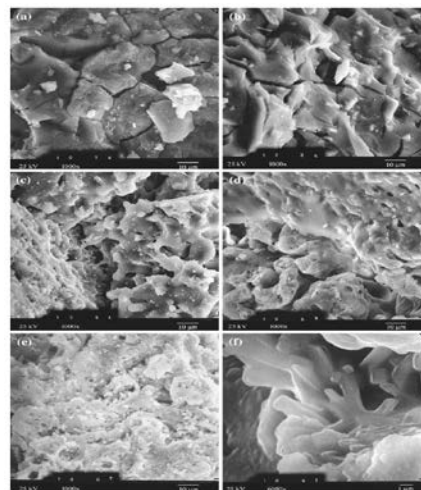
Figure 14. SEM Images of Alkali-activated Aluminosilicate After Thermal Loading to: (a) 25 °C, (b) 600 °C, (c) 800 °C, (d) 1,000 °C, (e) 1,150 °C, (f) 1,200 °C [36]

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Both compressive and bending strengths reached a minimum value at 800 °C exposure yielding at five times less for compression and 2.5 times less for bending than the control group absent from heat, yet additional loading to 1200 °C had a reverse affect, leading to an increase in both strength characteristics to within 12 percent and 18 percent respectively of the reference control specimens [39]. This is attributed to Akermanite ($Ca_2MgSi_2O_7$) formations which are observed forming at high temperatures and enhance mechanical strength.

Conductivity decreased under thermal load by approximately 30 percent at 600 °C and by 40 percent at the 800 °C mark; additional loading had no significant affect upon conductivity values [39]. Thermal conductivity reached its minimum value at 1200 °C, while both mechanical strength and porosity were at their respective maximums.

Porosity increases with increased thermal load and development of voided pores is thought to be a direct result of product degradation at extreme temperatures [40].

4.4.4. Curing Duration

Relative to Portland cements, geopolymers set rapidly and attain a significant percentage of their total compressive strength value within the first few hours of reaction. Temperature is especially important during the two- to five-hour interval; however, the strength increase for specimens cured beyond 48 hours was not significant [3]. Whereas Portland cement requires time to fully cure, the advantage of geopolymer cement product is the rapid set time characteristics. The rate of increase in strength was rapid up to 24 hours of curing time; beyond 24 hours, the strength gain was only moderate, thus heated curing time need not be more than 24 hours in practical applications [6].

Testing has shown that compressive strength values of 60 MPa can be achieved after only five hours at 85 °C [3]. Longer curing times will increase the strength of alkali-activated systems, but the gain will occur at a much slower rate as time progresses due to alkaline saturation and product densification. It is shown, however, that the mechanics can be well-enhanced via this trickle reaction. While short thermal activation periods of 2–5 hours produced Al-rich gels yielding lower mechanical strengths, extended curing to seven days promoted a change in the gel to a Si rich phase of much higher mechanical strength [10].

5. MICROSTRUCTURAL AND MINERALOGICAL PROPERTIES

This section discusses the microstructural and mineralogical characteristics of the hardened geopolymer cement matrix and identifies influential factors contributing to (or detracting from) enhanced mechanical performance. Detailed matrix analysis using XRD (X-ray Diffractometer), Fourier Transform Infrared Spectrometry (FTIR), Scanning Electron Microscopy (SEM), and ^{29}Si / ^{27}Al Magic Angle Spinning - Nuclear Magnetic Resonance (MAS-NMR) technologies allow quantification of minerals and measurement of inherent properties at a micro level.

5.1. Reaction Products

The resulting reaction product formed within alkali-activated geopolymers is defined by the prime materials used, the activating solution and the content of each entity. The main reaction product in fly ash activation under mild curing conditions of 60–90 °C is a three-dimensional aluminosilicate gel of amorphous nature with a predominance of $Q^4(3Al)$ and $Q^4(2Al)$ units [41]. The controlling mechanism of the reaction which generates this precursor gel is associated with the dissolution process by which the high concentration of OH^- in the system breakdown the vitreous phase Si-O-Si, Si-O-Al, and Al-O-Al bonds forming Al-OH and Si-OH groups which condense and give way to the precipitation of the short range zeolitic gel product [43].
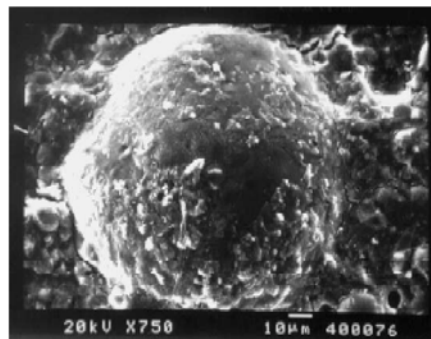
Figure 15. Fly Ash Particle Covered in Reaction Product Crust [41]

5.2. Porosity

The porosity of geopolymer cement is dependent upon several variables of the mix design. It bears direct significance to compressive strength properties of a given cement specimen and is heavily influenced by the activating solution type, concentration and the pozzolan material employed. The alkaline concentration of a given geopolymer binder is inversely proportional to its final porosity; an increase in concentration results in a less porous microstructure of enhanced strength capabilities [18]. Furthermore, GGBFS pastes are observed to possess larger volumes of porosity by comparison to ordinary Portland cement pastes [41]. The pH level of a paste mix also affects the porosity in the same manner by increasing the reaction degree, thus filling available void space with reaction product.

Thermal loading to extreme temperatures has a negative effect on geopolymer porosity. Porosity voids were shown to increase significantly at 600 °C with maximum voids detected at 800 °C [39]. Temperature loading between 800 and 1000 °C did not cause additional porosity changes in the specimens; however, loads to 1200 °C were found to exponentially increase porosity, and yet final compressive strength values did not suffer [39]. Additional testing by Bakharev showed that thermal loading to 1000 °C increased the overall pore volume by 3 percent (increased overall pore volume from 26–29 percent), yet nominal pore size increased from 37.6 nm (pre-loading) to 1835 nm after exposure, which was attributed to material decomposition upon heating [30]. Post-loading analysis revealed the formation of Na-feldspars

in the matrix. It was believed that the presence of unreacted sodium in the binder caused crystallization of the Na-feldspars upon firing and contributed to the increase of porosity and the deterioration of strength [40].
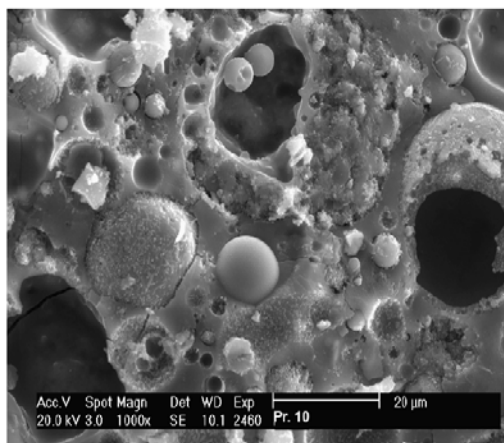
Figure 16. Porous Character of a Geopolymer Matrix at 28-day Hydration [7]

Under such conditions, the pore walls experience high stresses due to uncombined water expansion upon heating and the aluminosilicate gels deteriorate quickly. The loss in the strength combined with pore wall stress can cause the collapse of the pore and result in shrinkage cracking throughout the specimen [40].

5.3. Reaction Degree (α)

The degree of a reaction is a quantitative measure of particle reactivity within an alkali-activated geopolymer cement material. The most influential factor in pozzolan reactivity is the particle size distribution of the prime starting material [15]. Measurement of this reactivity is conducted using hydrochloric acid (HCl) to dissolve all reacted particles from the hardened matrix and quantify those absent from reaction. The acid solution dissolves the reaction products (aluminosilicate gels and zeolites) but does not significantly interact with unreacted ash particles [10].

The alkaline activator dissolves holes in the hollow pozzolanic particles, revealing additional smaller particles within, thus allowing further reaction to occur. Figure 17 illustrates this phenomenon. Chemical attack at one point on the particle surface causes expansion into a larger hole, exposing smaller ash particles contained within to bi-directional alkaline attack on both sides of the particle wall [44]. This allows for the reaction product to be formed both inside and outside of the spherical shell until the particle is completely consumed by the alkali forming a dense matrix of high compressive strength [44].
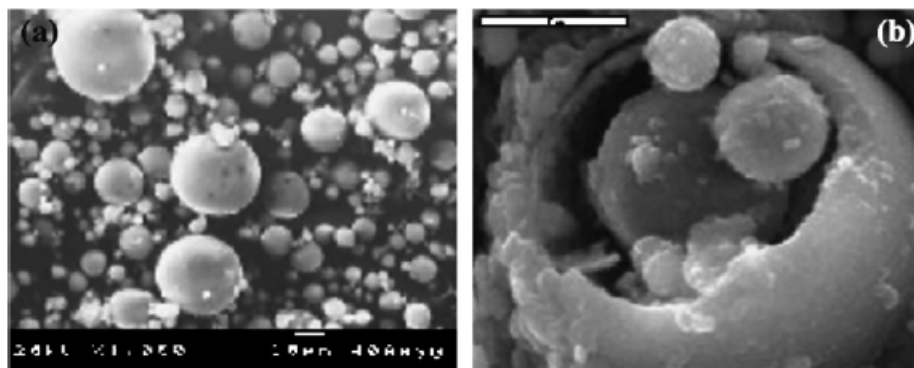
Figure 17. Alkali-activated Fly Ash Microstructure: (a) Original Fly Ash Spheres; (b) Dissolved Ash Particles Housing Smaller Particles Within [33]

The initial reaction rate of the binder matrix is rapid due to readily available pozzolan particles; however, the exponential formation of the hydrated gel product on the surface of smaller particles prevents potential reactivity due to full encapsulation by the semi-permeable crust. As alkaline activation continues, the unreacted particles buried under reaction product may not be affected by the high pH of the activator, thereby reducing the reaction rate over time [44]. The overall reaction degree and reaction rate of the system is a function of the formed product permeability and the diffusion of the alkali through the crust wall and onto the remaining ash particles.

5.4. Binder – Aggregate Interface

The weakest and most vulnerable of a concrete material lies within the aggregate-binder interface, or interfacial transition zone (ITZ). The transitional zone maintains a higher porosity than the surrounding paste matrix and therefore, it allows easier penetration of harmful chloride species into the concrete structure [26]. In Portland cement products, the ITZ consists of a higher concentration of the portlandite crystal and a lower concentration of calcium silicate hydrate (C-S-H) which is the main binding phase within the overall system [9]. However, no transition zone could be detected either morphologically or by direct measurement of the geopolymer product in the aggregate proximity [7]. Figure 18 identifies that lack of transitional interface zone in a geopolymer matrix; Figure 19 represents the same interface zone for Portland cement concrete.
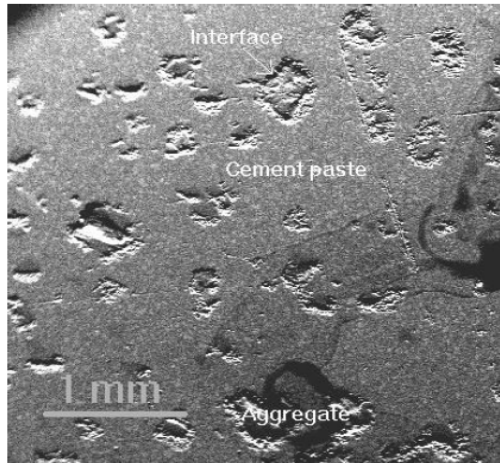
Figure 18. Geopolymer-aggregate Interface Zone [7]
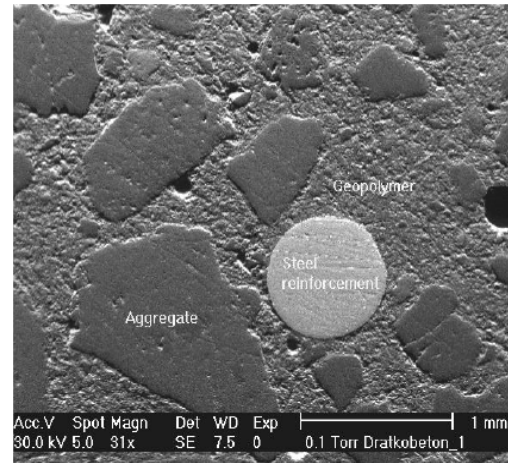
Figure 19. Portland Cement Concrete-aggregate Interface Zone [7]

High soluble silicate dosages in the binder mix reduce alkali saturation in the concrete pore solution and promote greater interparticle bonding within the geopolymeric binder as well as the aggregate mass [26]. The increase bonding forms a denser, stronger ITZ and a concrete of enhanced mechanical properties. This element of concrete production is critical in determining mechanical characteristics of geopolymer mortars and concretes [26].

6. MECHANICAL PROPERTIES

As previously discussed, the mechanical properties of geopolymer concrete are influenced by a variety of factors including curing temperature and duration, silicate/hydroxide ratio, alkali concentration, pH level, Si/Al, aluminum source, liquid-to-solid ratio, age of concrete and type of pozzolanic material utilized. In order to produce a geopolymer of high compressive strength, source materials which boast a high reactivity potential are required [3]. In this chapter, the mechanical properties of geopolymer materials are discussed and evaluated. The mechanical properties of geopolymer cement and concrete have the potential to be equal to or greater than those exhibited by similar Portland cement products.

6.1. Compressive Strength

Compressive strength values are shown to rapidly increase during the first few hours of reaction with additional, slower strength gain over an extended period of time. Initial reactivity is intense and occurs quickly upon activation, but reaction products eventually coat remaining unreacted pozzolan particles and reduce the efficiency of activation. As the activator slowly permeates through the newly-formed coating, the reaction continues at a slower rate, and compressive strength values continue to gradually rise. For this reason, the strength potential past 28 days is negligible and often is ignored.
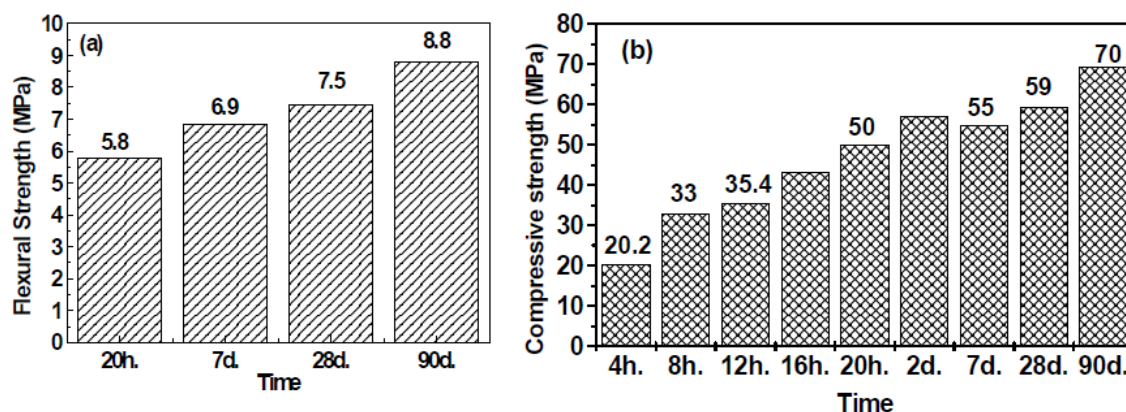
Figure 20. Compressive and Flexural Strength Gain of Geopolymers vs. Reaction Time [44]

The highest compressive strength values of 100–160 MPa were obtained from geopolymers on the basis of a fly ash and blast furnace slag mixture at a cure interval of 28 days [7]. The pozzolan mixture promoted a substantially smaller porosity in the range of 2–10 percent which maximized potential strength and fortified compressive properties. Figure 21 illustrates this point of enhanced performance from fly ash/slag mixtures.

Curing temperature increase promotes an increase in pozzolanic reaction; therefore, ambient temperature curing results in extremely slow reaction and elevated temperatures catalyze formation chemistry in the fresh paste. Temperatures in the range of 70–90 °C have a beneficial impact upon compressive strength in geopolymer cements [7]. As the added heat increases, the viscosity of the material is shown to increase exponentially, illustrating a connection between

temperature and reaction potential. This in turn, develops a relationship between viscosity and compressive strength. Viscosity indirectly indicates the compressive strength potential of a geopolymer paste [3].
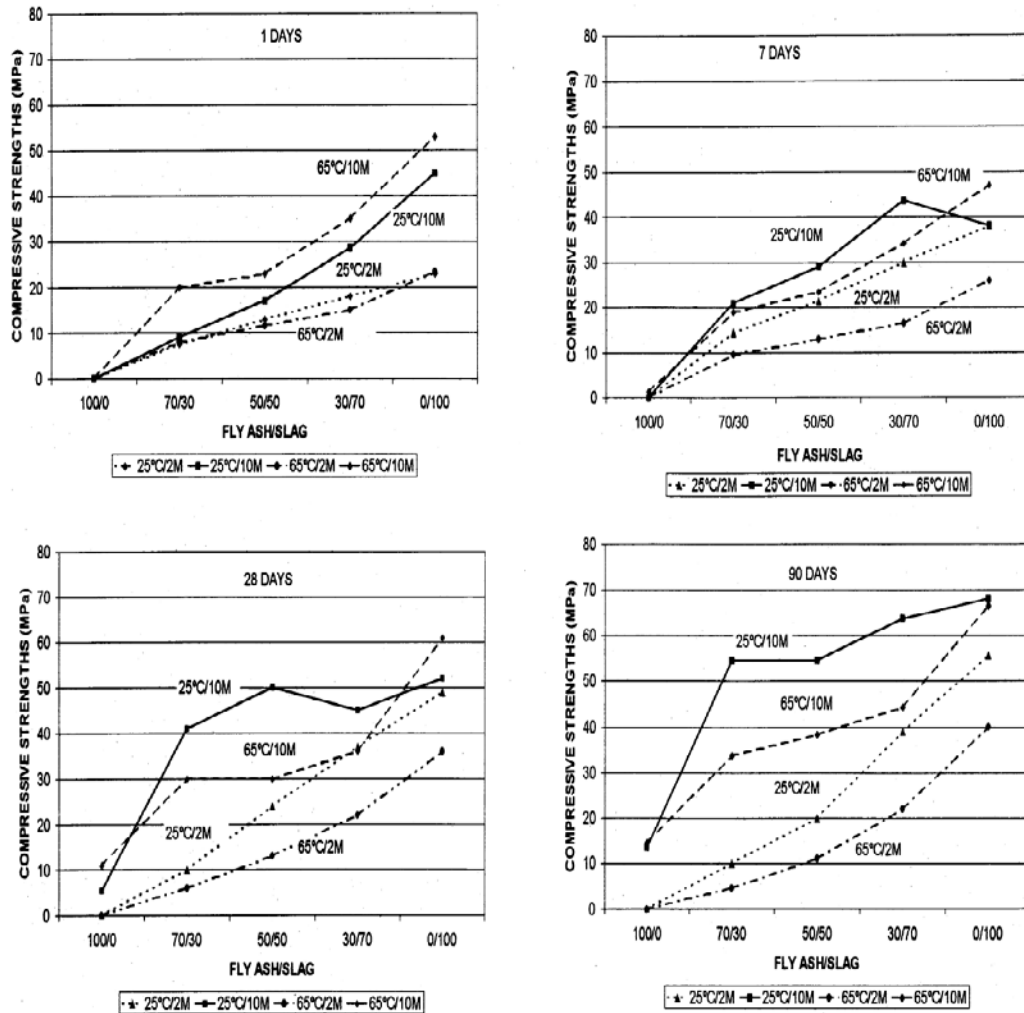
Figure 21. Compressive Strengths of Fly Ash/Slag Mixture at Various Ages and Alkaline Concentrations [26]

A water-to-solid ratio increase causes a decrease in available specimen strength, while geopolymers containing kaolin and/or metakaolin clays were found to be strongest under compressive loads [3].

6.2. Bending Strength

Not unlike other cementitious materials, the bending strength of geopolymer cements is far inferior to its compressive strength capabilities. As in the case of compressive strength, Portland cement-free activated ash concrete develops very high flexural strength at early ages, with gradual increases over time [3].

In agreement to observation, the ratio of compressive-to-tensile strengths under bending loads is measured in the range of 10.0:5.5 for geopolymers, while cement-based concretes typically possess maximum ratios of 10.0:1.5 [7]. The benefit of such an increased tensile potential suggests a possible reduction in reinforcement quantity for structural elements of identical geometry.

6.3.   Toughness

While geopolymer mortars and concrete products have proven to be mechanically sound and resistant to many harsh chemical compounds, the hardened material remains quasi-brittle and require the aid of mechanical reinforcement to maintain service longevity and afford the barrage of elements present in commercial use. Research has been completed to identify the affects upon geopolymer materials from the inclusion of inorganic fiber materials to enhance toughness characteristics and overall concrete durability.

6.3.1.   Fiber Reinforcement
The addition of manufactured fiber material as reinforcement is an efficient method to improve the toughness of brittle materials and provide mechanical stabilization to an otherwise non-uniform system of low mobility [46].

6.3.1.1.   Short Fibers
The addition of short polyvinyl alcohol (PVA) fibers reinforced geopolymer composites and resulted in good flexural strength and reasonable toughness, while adding short basalt fibers reduced the strength of tested specimens and drastically improved the work of fracture element [47]. Research shows that a 10 percent incorporation of short fiber material could increase the flexural strength of geopolymer composite by 224 percent [47]. The homogeneity of the fiber material can be ensured through the employment of ultrasonic scattering technology.

Short fibers maintain the advantage of possessing high modulus and strength characteristics, low thermal expansion, and excellent electrical properties. They have also been used to facilitate heat transfer and improve mold stability in geopolymer cements [47]. The addition of 3.5 percent of short fiber material increased specimen strength by a magnitude of 4.4, yielding value increases from 16.8 to 91.3 MPa [47].

The length of each short fiber is directly related to potential load transmission and interfacial fiber/matrix cohesion within the matrix. The longer fibers impart more restriction on deformation; whereas shorter fibers create added friction due to the increased number of available fiber ends [47]. Fiber bridging and pull-out resistances are the main mechanics behind the strength and toughness enhancement. It is this fiber-to-matrix debonding under tensile stress and subsequent fiber pull-out that consume the fracture energies and prevent catastrophic failures during service life [47].

6.3.1.2.   Long Fibers
Long fibers provide mechanical stability and toughness from a different perspective than those identified for short fiber material. The added length can be both an enhancement factor and detriment to improved cement functionality and toughness. The longer fibers can sustain greater tensile forces prior to pull out due to their ability to endure additional stress-induced elongation

while still maintaining bond strength from the fiber ends absent from tensile forces. As the matrix along the tensile side begins to expand under load, the longer fibers can absorb some of these energies elastically and offer the system a higher plasticity prior to final pull out and failure. Conversely, longer fibers can become more easily entangled within the matrix, thus causing a factor of redundancy to exist and lowering available toughness potential altogether. A fiber length of 7 mm is identified as the critical length, essential for the production of geopolymeric materials with optimum reinforcement and improved toughness [47].

6.4.   Steel Adhesion

An interesting property of geopolymer cements is their ability to form an extremely strong bond with steel products. Pull out testing has concluded that the bond strength between this alkaline concrete mix and steel reinforcement is so great that 8 mm bars embedded in the matrix broke in two prior to experiencing slippage or concrete cracking [2]. Additional samples did not cause steel failure, but the loads being applied to cause bar slippage were 12 MPa and 17 MPa, respectively. This not only surpasses the 9.70 N/mm requirement specified in the Spanish concrete code (EHE) as the minimum load to pass the beam test [2], but it signifies the intense bonding characteristics of alkali-activated cement systems.

7. DURABILITY

Geopolymer cements are inherently resistant to chemical attack and thermal loading due to their reduced porosity and thermal conductivity characteristics. Many of the durability problems associated with PCC arise from its calcium content in the main phases [25]. The C3A reacts with sulfate ions in the presence of $Ca(OH)_2$ to form ettringite and gypsum, which in turn cause expansion and degradation of the cement into a non-cohesive granular mass [25]. It is the low calcium content found within pozzolanic materials that prevents geopolymers from experiencing such negative effects.

While geopolymeric materials possess an enhanced level of durability over Portland-based cements, they are not completely immune to environmental threats. Immersion in seawater slightly affects internal porosity as a result of Na ions being replaced by Mg ions in the gel microstructure. Highly acidic media cause a de-alumination to occur in alkali-activated cements, thus resulting in loss of mass and a decline in mechanical strength. It is noted, however, that the strength loss in comparison to PCC is much less.

7.1. Chemical Durability

Research shows that geopolymer materials can easily withstand months of immersion in a variety of aggressive elements without experiencing any form of deterioration and/or surface alterations as typically found with Portland cement-based products. High alkalinity boasts a higher degree of reaction and maintains a matrix density that tends to prohibit the permeation of corrosive elements into the internal framework of geopolymer cements.

7.1.1. Sulfate Resistance

Heat-cured, low calcium fly ash-based geopolymer concrete exhibits high resistance to sulfate immersion and attack. Specimens exposed to sodium sulfate for up to one year showed no visual signs of surface deterioration, cracking or spalling [6]. Compressive strength values remained equivalent to those obtained prior to immersion. Moreover, shrinkage was insignificant, measuring less than 0.015 percent from initial geometry [6]. Little change in visual appearance and no significant formation of reaction products can be witnessed in the specimens shown in Figure 22.

Figure 22. Geopolymer Mortar After 1.5 Years Exposure to MgSO$_4$ and NaCl Salt Solutions [6]

Whereas Portland cement-based materials inherently form expansive ettringite and gypsum crystals as a result of prolonged sulfate contact, the main product of geopolymer cement is absent of these elements, and therefore, little to no forced expansion is expected. The only threat of such formations within geopolymers stems from the possibility of high calcium in either the utilized pozzolanic material or included aggregate material.

7.1.2. Acid Resistance

Geopolymers are not as resistant to acidic solutions as they are to sulfate attack described above. However, the maximum loss of test specimens was observed at three percent after one year in a two percent sulfuric acid solution, which is negligible when compared to the complete degradation of Portland cement-based control groups [6]. The extent of damage associated with acid exposure is directly proportional to acid concentration of the immersion solution.

Testing performed by Davitovits revealed complete destruction of Portland cement-based specimens in the

Figure 23. Geopolymer Concretes After One Year Sulfuric Acid Exposure [4]

presence of five percent HCl and H_2SO_4 solutions; no significant change in mass, length or compressive strength was measured for the geopolymer samples subjected to identical rigors [3]. However, subjects immersed in testing shown in Figure 23 display slight degradation in higher concentrations of sulfuric acid after a one year exposure time. The severity and distortion of specimen shape is directly related to the concentration of the bath solution [4].
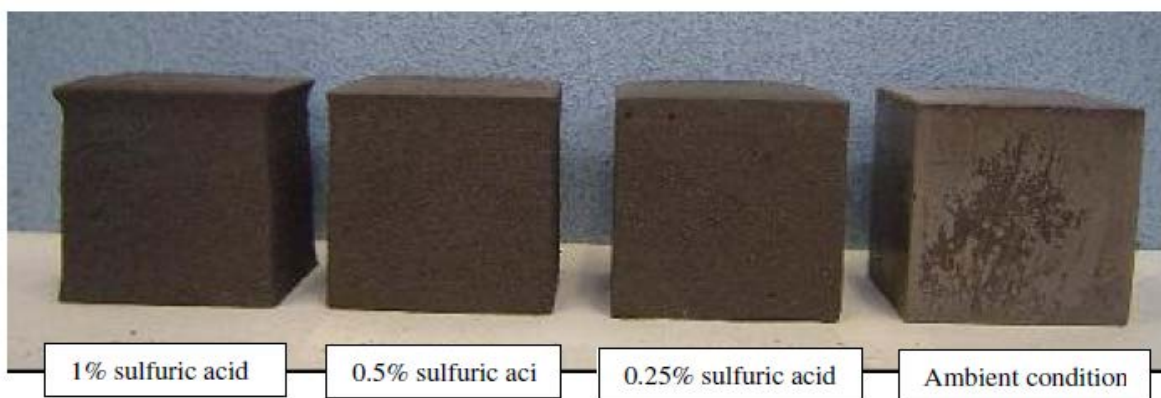
Figure 24. Geopolymer Mortars Subjected to One Year Sulfuric Acid Exposure [4]

7.1.3. Alkali-Silica Reactivity (ASR)

ASR is a chemical process between an alkaline solution and the aggregates involving alkaline oxides in the cement and forms of reactive silica present within the aggregate. This process ultimately results in dissolution of the aggregate mass [31]. Minerals such as opaline, cryptocrystalline silica, chalcedony and microcrystalline quartz are considered to be potentially reactive and can cause ASR-induced expansion when placed into contact with the correct proportion or concentration of reactive aggregate [31].
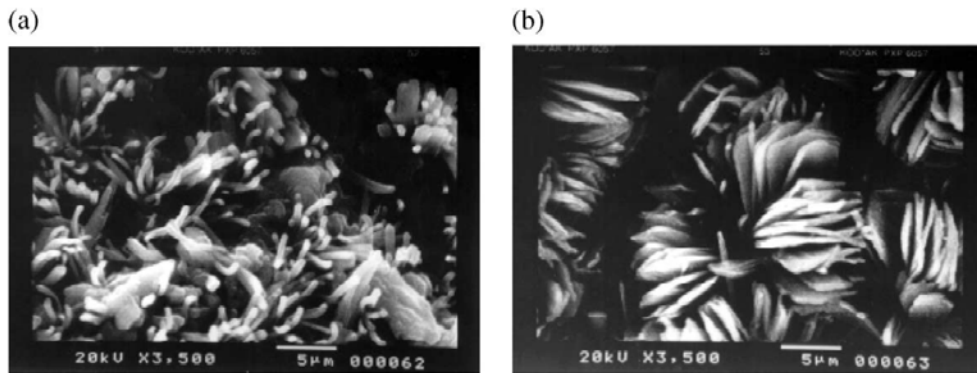
Figure 25. AAS Mortar Stored in 1M NaOH Solution at 80°C for 140 Days

The ASR expansion is more of a concern in PCC due to the presence of portlandite ($Ca(OH)_2$) in the Portland cement paste [49]. The portlandite reacts with activator alkalis (NaOH, KOH) under favorable humidity conditions to form a gel which eventually morphs into a rigid crystalline structure causing internal expansion and deterioration of the cementitious mass. The chemical equation of a typical alkali-silica reaction is outlined by Fernandez-Jimenez and Puerta [27] as follows:

$$Ca(OH)_2 + SiO_2 + NaOH + H_2O \rightarrow n_1Na_2O \cdot n_2CaO \cdot n_3SiO_2 \cdot n_4H_2O$$
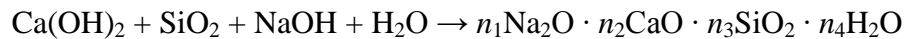
The resulting gel will have an expansive nature relative to the content of CaO in the final product [36]. GGBFS and fly ash have been used in PCC designs to minimize potential destruction caused by ASR expansion by reducing the amount of portlandite in the mix.
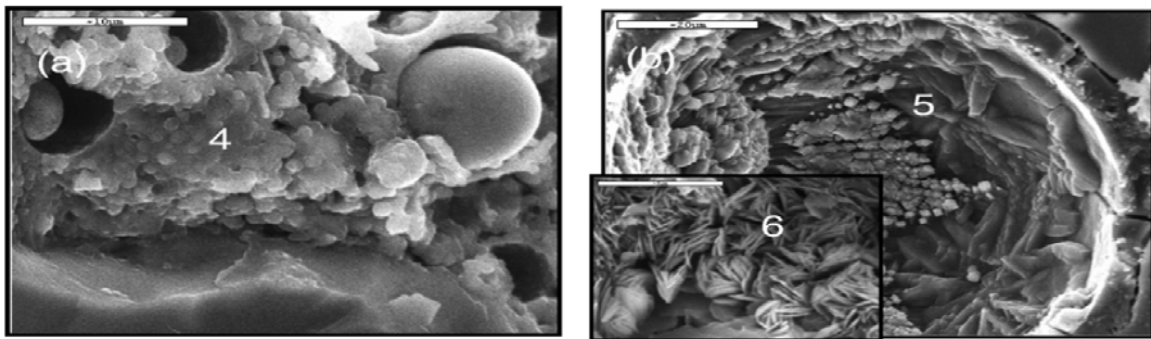
Figure 26. Photomicrograph of an Activated Fly Ash Mortar: (a) 16 Days Post-activation, (b) Zeolitic Crystalline Formations at 90 Days of Hydration, (6) ASR 'Rosette-type' Morphology [34]

7.2. Heat Resistance

Under extreme heat loading, geopolymers exhibit a morphological ability to form a new microstructure based on akermanite (rather than the initial C-S-H product) which possesses superior mechanical and thermal resistance properties making it a prime candidate for fire protection materials and reinforced concrete structures.

Geopolymers under heat loading do not release toxic fumes, experience low weight loss in the range of 5–12 percent (as compared with 50–80 percent for fire resistant polymer nanocomposites) and are nonflammable in the presence of temperatures to 1000 °C [40].

The fire resistance of geopolymer materials is far superior to those created using Portland cement. In support of this claim, research shows that a 10 mm thick geopolymer concrete panel exposed to a flame in excess of 1100 °C produced reverse-side temperature measurements of only 240–283 °C after 35 minutes of continual testing [3]. Evidence suggests that the increase of KOH concentration and the addition of metakaolin could further decrease the thermal conductivity.

7.3. Freezing and Thawing Resistance

Geopolymers are also resistant to the effects of repetitive freezing and thawing cycles. The compressive strength values of specimens subjected to 150 freeze/thaw cycles were observed to drop by only 30% of original test values absent from freeze exposure [7]. On this basis, geopolymers have proven to be highly resistant to both temperature extremes. The specimens in Figure 27 represent three separate geopolymer mix designs after exposure to low thermal extremes in freeze/thaw cyclical testing regimes.
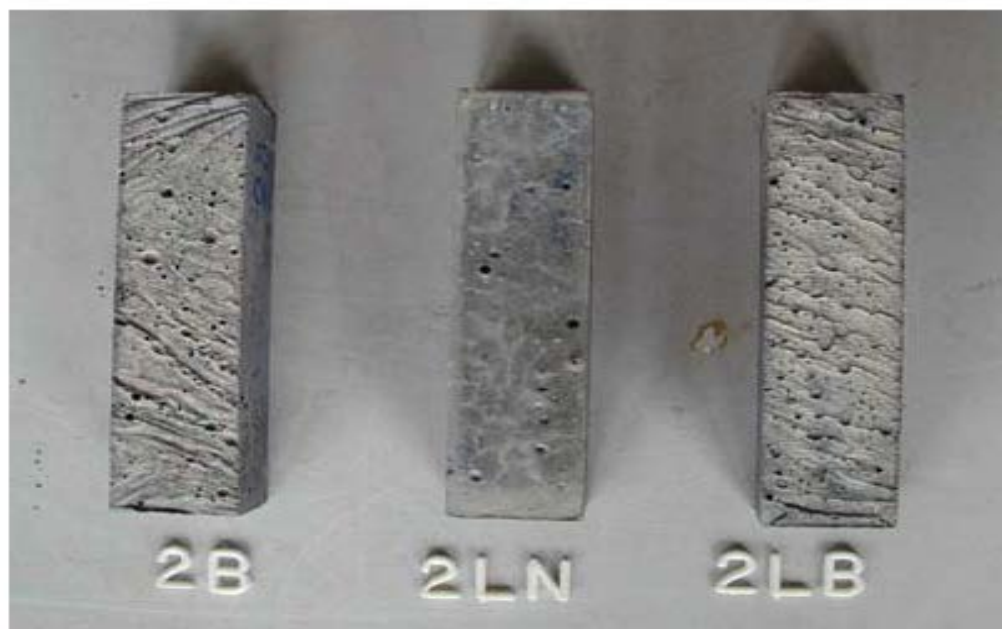
Figure 27. Geopolymer Mortar After 150 Freeze/Thaw Cycles [7]

8. ADVANTAGES AND DISADVANTAGES OF USING GEOPOLYMER CEMENT CONCRETES

8.1. Advantages

Many advantages of using alkali-activated geopolymer cements for commercial concrete production in lieu of PCC have been reported in the literature. These are summarized below.

8.1.1. Economic Benefit

The production of geopolymer cement reduces the demand for costly production of the clinker required in Portland cements. The high cost of Portland cement production stems from the vast amount of energy required to produce the material. The exceptionally high temperatures (1400–1500 °C) required for Portland cement production make this a very costly and energy-intensive process [31].

The pozzolanic materials used in geopolymer cement are readily available as by-products of industrial coal power plants and are therefore inexpensive to attain. As of the year 2005, Fernandez-Jimenez *et al.* reported that only 30–40 percent of available fly ash material is being utilized leaving the rest to be disposed of through environmentally controlled processes to mitigate the risk of air pollution, leaching and potential pollution of inland and marine waters [48]. To alleviate this growing problem through recycling into commercial construction materials would not only be economically sound but responsible to the environment as well.

8.1.2. Environmental Benefit

The production of geopolymer concrete serves to reduce environmental concerns for Portland cement production on a two-fold basis. Simply by replacing Portland cement as a commercially - viable substitute, the CO_2 emissions generated during Portland cement production would cease to exist. The production of one ton of PCC emits approximately one ton of CO_2 into the atmosphere [6]. For this quantity of Portland cement, 2.8 tons of raw materials are required, including fuel and other materials, and production creates 5–10 percent of all airborne dusts [3]. Furthermore, the utilization of unclaimed pozzolanic by-products from power plants worldwide would prevent these materials from being disposed into the environment in their hazardous, raw state. Currently, unclaimed fly ashes and blast furnace slag are deposited into landfill facilities increasing the risk for leaching metals into groundwater; geopolymer cement production on a global scale would reduce this risk. Using geopolymer concrete in lieu of PCC would save 0.25 million tons of coal, 80 million power units and prevent 1.5 million tons of CO_2 from entering the atmosphere [50].

8.1.3. Chemical Resistance

It has been shown that geopolymer cements possess excellent resistance to sulfates and various acids. The deterioration of Portland cement from sulfate attack is attributed to the formation of expansive gypsum and ettringite which causes cracking and spalling in the concrete. The superior performance of geopolymeric materials in acidic environments is attributed to the lower calcium content of the source material [6]. Geopolymer cement produces no gypsum or ettringite formation, therefore no mechanism of sulfate attack in heat-cured, low-calcium fly ash based geopolymer cement is observed [6]. The exposed specimens in Figure 28 support this theory.

Cured specimens immersed in solutions of sodium chloride (NaCl) and $MgSO_4$ salts for a period of 1.5 years showed no visual signs of corrosion products, and x-ray diffraction analysis after a two-year period failed to identify the presence of expansive hydration products [7]. While a geometric expansion of 0.5 percent from sulfate attack is considered failure, Khale and Chaudhary report a sample length change of less than 0.02 percent over a 24 week exposure period. Furthermore, metakaolin-based geopolymer mortars showed negligible deterioration in microstructure and strength after being immersed in seawater, sodium sulfate and sulfuric acid solutions [3]. Additional sulfuric acid testing by Rangan showed only a three percent mass loss of the geopolymer specimen as compared to complete destruction of Portland cement samples tested by Khale [6, 3].

Figure 28. One-Year Visual Appearance of Geopolymer Specimens Exposed to [l-r]: 5% Na_2SO_4; Fresh Water; Ambient Condition [45]

8.1.4. Thermal Stability

Geopolymer cements have been found to possess excellent resistance to temperature extremes. Samples exposed to 150 freeze/thaw cycles retained 70 percent of their original compressive strength [7]. Alternatively, specimens exposed to extreme temperatures of up to 1100 °C lost a maximum of 60 percent of their residual strength in the range of 500–600 °C, but it was reported that post-firing geopolymer samples still remained stronger than those of a Portland cement mix design [1]. Bending strength tests performed by Fernandez-Jimenez and Palomo observed only a 33 percent decrease in geopolymer strength during exposure to temperatures of 1000 °C, while the recorded strength of samples containing Portland cement fell to nearly zero beyond the 600 °C interval [51]. Compressive strength values reported from the same series of experiments were far greater for the fly ash-based specimens than for those of Portland cement. Residual compressive strength for the Portland control fell to near zero at temperatures beyond 800 °C, while activated ash material maintained constant residual strengths between 800 and 1000 °C regardless of curing method [52]. Figure 29 shows a significant increase of compressive strength at 1000 °C. Zuda et al. observed a two-fold increase in compressive strength and a six-fold increase in bending strength as a result of 1200 °C exposure temperatures. Material characterization analysis using microscopic technologies have identified the crystallization of the mineral akermanite ($Ca_2MgSi_2O_7$) as the main reason for such high temperature resistivity [53].
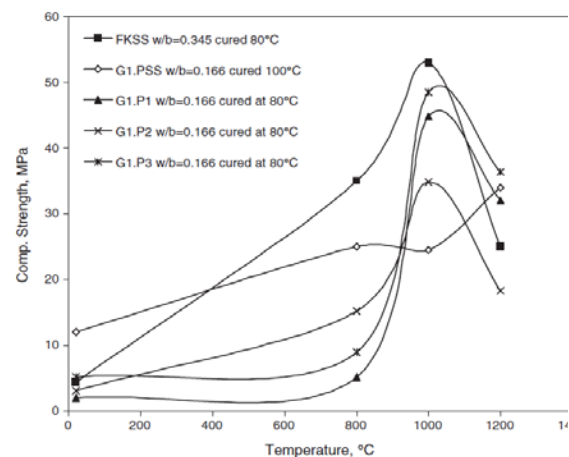
Figure 29. Compressive Strength Characteristics of Geopolymers Under Extreme Thermal Loading [39]

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8.1.5. Minimal Shrinkage

While it is reported by Skvara et al. that no shrinkage due to reaction takes place in geopolymers and the dimensional characteristics of the fresh paste remain preserved as a permanent value [7], others have observed significant shrinkage to unacceptable levels. Wallah and Rangan reported only 100 microstrains of dry shrinkage strain during a one-year period for all test specimens. Conversely, it was observed that ambient-cured specimens developed exponentially higher shrinkage within the first two weeks as a result of slow evaporation relative to those cured under heated conditions [4]. Figure 30 shows the difference between heat-cured and ambient-cured microstrain, while Figure 31 compares steam heating and dry heating as two different curing methodologies.
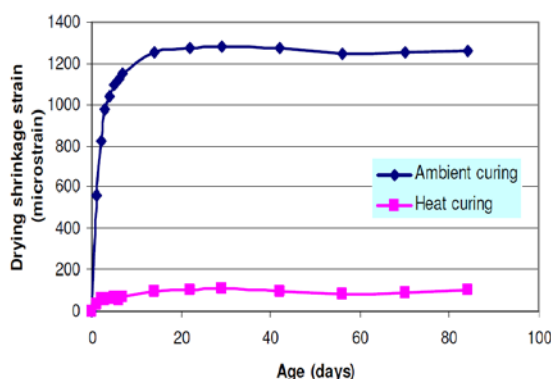
Figure 30. Ambient vs, Heat-cured Dry Shrinkage [4]
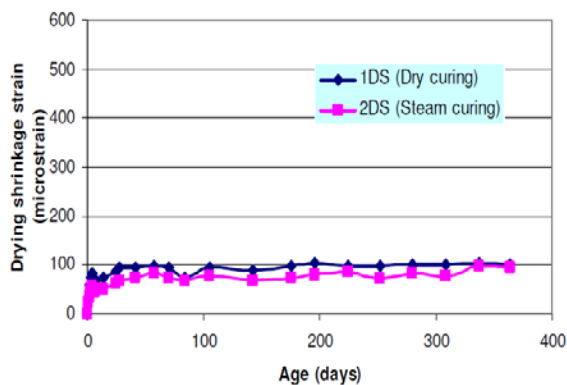
Figure 31. Dry Heat vs. Steam-cured Dry Shrinkage [4]

8.2. Disadvantages

8.2.1. Pozzolan Composition Analysis

The chemical composition and the particle size distribution of the fly ash must be established prior to use [6]. The mechanics of hardened geopolymers are directly related to the mineralogical composition of the selected pozzolan. Slight variations in these materials have significant affects upon the resulting binder properties. The amount and form of calcium in the raw play significant roles in determining the reaction pathway and the physical properties of the final product [5]. Prior to activation, a micro-analysis of the pozzolan must be performed to identify minerals present and their quantity relative to the overall mass. This will dictate the proper activating agent to be used and the concentration required to achieve optimum reaction. In fly ash, silica content is usually found to account for 40–60 percent of the ash material, alumina from 20–30 percent, and iron presence varies widely [3].

The fineness of the ash is also critical in mechanical strength development; to wit, 70 MPa values have been observed in pastes derived from ashes with a particle size of less than 45 μm. Fly ash particles are inherently non-homogeneous; therefore, care is required to ensure an optimal mix design and a consistent final product [5]. These factors are highly relevant to the overall development of geopolymer cements and must be analyzed in detail prior to a finalization

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of mix design. Understanding the structure and dissolution properties of the pozzolanic material is central to the commercial application of geopolymer cements [5].

8.2.2. Decreased Workability

The rheological properties of geopolymer cements are different from those found in Portland cement concretes. Pozzolan-based geopolymer cements possess higher static and dynamic viscosities than Portland cement products and can require vibration efforts to minimize entrained air pockets in the fresh paste [7]. Superplasticizers are also a viable solution for a stiff mix, but provisions to the mix design must be made accordingly to avoid ratio upsets. The addition of naphthalene sulphonate-based superplasticizer, up to four percent of the fly ash by mass, improves the workability of the fresh geopolymer; however, dosages greater than 2 percent can cause slight degradation of compressive strength in the hardened product [6].

9. COMMERCIAL APPLICATIONS OF GEOPOLYMER MORTARS AND CONCRETES

Geopolymer mortars and concretes possess a high potential for use in commercial applications due to their enhanced durability, thermal and chemical resistance properties, rapid development of mechanical strength, adherence to reinforcements/aggregates and economic benefit as an industrial by-product material. Compressive strength values over 70 MPa within 24 hours and high resistance to sulfates and various acids allow geopolymer materials to bear potential for a variety of commercial applications and industrial use.

9.1. Concrete Pipes

The use of geopolymer concretes for commercial sewer piping is a viable option from the basis of their inherent resistance to sulfates and acidic products. Sulfuric acid is generated in conventional sewer systems through the breakdown of hydrogen sulfide by aerobic bacteria in the system and is the main factor in corrosion and structural deterioration of the piping networks over time. Approximately 40 percent of the damage to PCC pipes can be attributed to corrosion by biogenous sulfuric acid attack as a result of long flow periods and insufficient ventilation of wastewater [36].

An additional concern regarding concrete longevity is acidic soil in the area of installation. Acidic sulfate soil contain naturally-occurring iron sulfides, mineral iron pyrite (FeS_2) or sulfide oxidation products and maintain pH levels between 1 and 4 which cause major damage to conventional Portland cement-based concretes. The aggressive acidic environments generated in acid sulfate soils have a serious impact on concrete and steel infrastructure and can lead to structural weakness and eventual failure [36]. Geopolymer concrete products are aptly suited to withstand the rigours of a sulfate environment and would offer an economic alternative to currently employed materials and the issues associated with regular repair of the piping networks.

9.2. Structural Elements

Research has been conducted to better understand the properties and mechanics of geopolymer materials and their potential for use as structural elements for construction. Currently, PCC is the preferred concrete material for buildings and structures, but its consumption of natural resources and energy portend the introduction of geopolymers into the industry. The increasing worldwide production of PCC to meet infrastructure developments indicates that concrete will continue to be the chosen material for construction in the future [38]. A motivation for research into to geopolymer cements is an attempt to produce an environmentally friendly concrete out of industrial by-products that would be capable of equaling or exceeding the mechanics and durability of traditional PCC products. In this light, much research has been conducted to determine the applicability of geopolymer columns and beam in lieu of PCC-based structures.

Figure 32. Geopolymer Columns After Demolding [52]

The load capacity of geopolymer columns is influenced by load eccentricity, concrete compressive strength values and longitudinal reinforcement ratios [50]. Decreased eccentricity loading and reinforcement ratio increases favor an increase in overall column load capacity. From the perspective of material longevity in harsh environments and large operating loads, geopolymer concretes are viably sound as they possess high compressive strength, experience very minor dry shrinkage and creep and maintain excellent resistance to sulfate attack and acidic immersion.
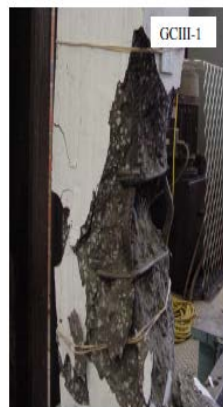
Figure 33. Geopolymer Columns After Demolding [52]
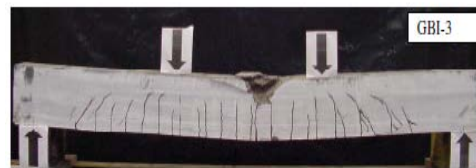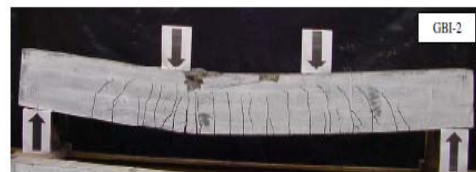
Figure 34. Crack Patterns and Failure Mode of Geopolymer Beams [52]

Failure loading of columns with smaller load eccentricity, higher strength and greater reinforcement ratios produced sudden, explosive fractures with short post-peak behavior with cracking widely opened near failure [50]. The failure zones were generally located between mid-height and up to 25 cm above or below column the mid-height axis [50]. Maximum capacity was

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observed to be 1559 kN with 15 mm eccentricity applied to columns produced using 66 MPa cement and 8N12 bars at a 2.95 reinforcement ratio [50].
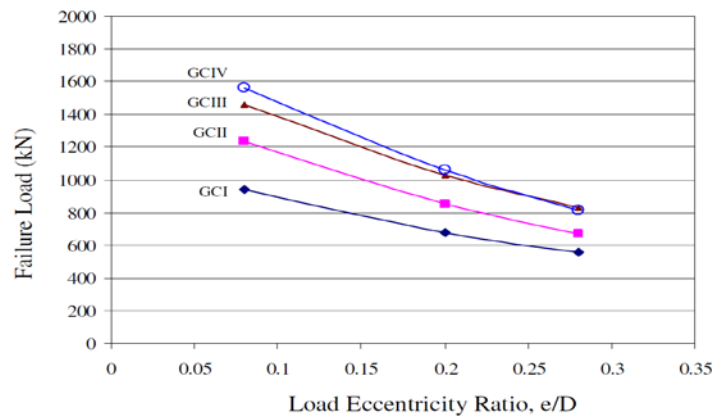
Figure 35. Effects of Geopolymer Column Load Eccentricity [52]

9.3.   Heat Resistant Pavement

The thermal capacity observed in geopolymer concretes makes them a viable possibility for heat resistant pavement applications. Pozzolan-based geopolymer cements do not readily decompose when exposed to high temperatures and appear to be more structurally stable under such conditions than PCC [51]. Geopolymer cements utilize more and store less water from solution during particle reaction, and therefore, prevent aged dry shrinkage and strength degradation due to rapid water loss under extreme heat. Fly ash-based cements retain their mechanical properties up to 600 °C, because their structural deterioration under these harsh conditions is much less pronounced than in Portland cements [51]. In addition, flexural plasticity is observed in geopolymer cements above 500 °C, where Portland cements become brittle and degrade. Its ability to remain dimensionally stable under extreme temperatures arises from a propensity for the material to recrystallize available hydroxysodalites into heat resistant minerals such as nepheline ($NaAlSiO_4$), albite and other anhydrous aluminosilicates to aid in heat resistance [51].

9.4.   Toxic Metal Immobilization

Geopolymer cements possess a high potential for toxic metal immobilization due to their inherently dense microstructural development. Low permeability is one of the properties that favors the use of these materials as immobilization systems for metals [45]. The geopolymer network encapsulates the metal elements either physically by trapping them in voided pore space in the solid matrix or chemically via charge balance with available anions in the atomic framework. Figure 36 represents the capabilities inherent within geopolymers to immobilize these hazardous metal elements.
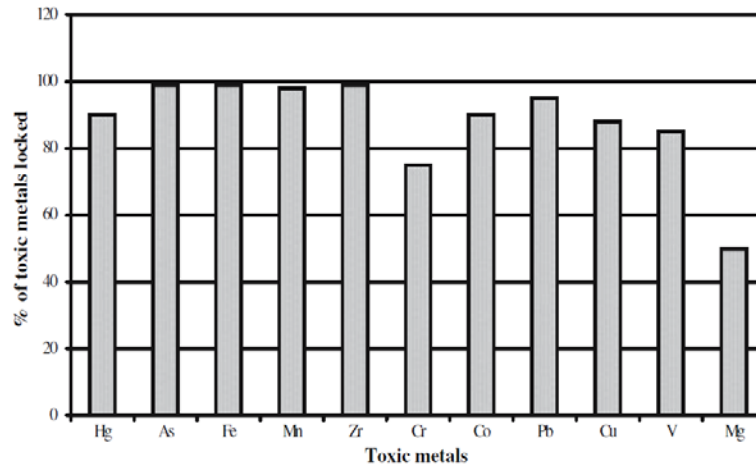
Figure 36. Geopolymer Toxic Metal Encapsulation Potential [3]

Research testing by Luna *et al.* concluded that the characteristics of leachability of a given geopolymer cement could not be related to its compressive strength [45], but all geopolymers tested showed excellent immobilization of selected metals (Pb, Cd, Cr, Zn). Samples prepared with a mixture of sodium silicate ($NaSi_2$) and potassium hydroxide (KOH) yielded the best results for these metals. Conversely, specimens containing kaolin and metakaolin exhibited excessive leaching and are not recommended for toxic metal encapsulation. Additional research is required to safely introduce geopolymers as materials for metal immobilization; however, the potential for such application is present.

9.5. Sub-aqueous Seawater Applications

The sulfate resistance characteristic of geopolymer cement material makes it a prime candidate for subaqueous marine applications. Mortars and concretes produced with alkali-activated metakaolin perform very stably when immersed in aggressive solutions of various types (deionized water, seawater, sodium sulfate solution and sulfuric acid) [25]. It is the ordering of the aluminosilicate gel that denoted each geopolymer's ability to tolerate aggressive environments; sodium hydroxide activated geopolymers are more crystalline than those prepared with sodium silicates and therefore are more stable and resistant to these harsh environments.

10. CONCLUSIONS AND RECOMMENDATIONS

10.1. Conclusions

The premise of geopolymerization is a fairly new idea, and commercial implementation is in its infancy. However, this new technology shows great potential for application in conventional construction as well as for construction in harsh and demanding environments such as high temperature applications and locations subject to chemical attack. Research to date has failed to clearly identify a proven formulation for each specific application.

The characteristics observed to date reflect properties typically reserved by traditional Portland cement binders and concretes. Compressive and bending strengths are in line with PCC. Thermal loading in excess of 1000 °C has been found to have little effect upon the internal matrix products of geopolymer materials. Sulfates and acidic agents have difficulty permeating into the densely formed aluminosilicate network which prevents potential degradation and structural failure as commonly witnessed in PCC products under the same rigors.

The pozzolanic materials required for alkali-activation are readily-available on a global level, and the cost-to-benefit ratio for the utilization of industrial waste is exceptional in relation to traditional cementitious products used in the industry today. As a product known for its ability to sustain the environment while maintaining durability and structural integrity under severe conditions, geopolymer concretes are being proven as a worthy substitute for traditional methods of cementitious production and field application.

The following summarizes notable characteristics of geopolymerization and highlights its effectiveness as a viable construction product for the future:
- Compressive and bending strength values of geopolymer concretes are similar to specimens constructed of Portland cement, yet the reaction products in geopolymer concretes exhibit no major strength loss during excessive thermal loads.
- Resistance to sulfate and acidic agents is attributed to the naturally low porosity within the geopolymer matrix. Smaller entrained air voids prohibit agent mobility and yield denser, stronger cementitious product. This resistance prevents the formation of ettringite and gypsum which can lead to cracking and eventual deterioration. This resistance to sulfate attack makes them a prime candidate for use in sanitary sewer design and concrete culverts. The constant presence of deteriorating liquids and gases in sewer pipes has been found to significantly erode conventional pipe walls over extended time periods. The service life of geopolymer concretes under these conditions would be far superior to pipes constructed of Portland cement.
- Since the primary ingredient of geopolymers is an industrial by-product (fly ash), geopolymers are relatively inexpensive to produce. Furthermore, the production of geopolymer cements does not generate harmful greenhouse gas emissions and is therefore considered environmentally friendly.
- Geopolymers do not require extended cure durations normally necessary for Portland cement-based materials. The initial degree of reaction and subsequent strengthening is rapid in alkali-activated systems, and cure durations between two and seven hours can produce a hardened material with excellent compressive strength capabilities.

- Hardened geopolymer materials do not allow significant heat transfer and perform well in extreme heat environments as fire retardant concretes and thermal barriers. Under such thermal load, geopolymers do not exhibit significant strength losses and maintain structural integrity.
- In general, fly ash-based systems experience little-to-no dry shrinkage during the cure process. Dimensional stability is a critical factor in concrete durability, and traditional cementitious materials tend to exhibit significant reduction volume as a result of reaction water losses. Geopolymers maintain much of their moisture during reaction, and the result is negligible mass loss.
- The formed matrix within an alkali-activated system possesses the ability to encapsulate heavy metals and prevent hazardous leaching to surrounding environments. This inherent property of geopolymer concretes is proving invaluable as a viable material for waste management.
- The matrix of a geopolymer under excessive thermal load becomes slightly plastic and can endure greater bending moments than the highly brittle materials based on Portland cement, thus reducing the design criteria for reinforcement under equivalent load. The thermal resistance of geopolymer concretes and their inherent capability to retard thermal conductivity promote their use in precast wall panels for fire protection. Temperatures beyond 1200 °C have been imposed onto geopolymer specimens without any visual or micro-visual sign of deterioration, and the surface temperatures opposite the heat source were magnitudes lower by comparison.

10.2. Recommendations

AFRL should invest resources (as available) to investigate geopolymer cements and concretes for two significant military-unique requirements:
- Material development meeting the Aircraft Operating Surfaces (AOS) unique requirements;
- Material development meeting airfield damage repair (ADR) requirements.

The technical objectives for the recommended research are listed below.

10.2.1. Technical Objective 1: AOS Material Development
- Compressive strengths greater than 6000 psi (41 MPa) at ambient temperature and greater than 3500 psi after one hour exposure to 1700 °F (900 °C) in the near term and far-term heat resistance greater than 2100 °F (1150 °C).
- Flexural strength greater than 750 psi (5.2 MPa), elastic modulus greater than 6×10^6 psi (41.3 MPa), and coefficient of thermal expansion (less than 2×10^{-6}/ °C).
- Working time between two and four hours.
- Maintain physical integrity (shrinkage/expansion less than one percent and compressive strength greater than 4500 psi (31 MPa) after six 30-second exposures to 1700 °F (900 °C).

10.2.2. Technical Objective 2: ADR Material Development
- Bond strength to substrate greater than 1000 psi (6.9 MPa).
- Compressive strengths greater than 4500 psi (31 MPa) at ambient temperature.

- Flexural strength greater than 750 psi (5.2 MPa), elastic modulus less than 4×10^6 psi (27.6 MPa), and coefficient of thermal expansion (less than 1×10^{-6}/ °C)
- Working time between one and two hours.
- Set time less than four hours (threshold) at ambient conditions, less than one hour (objective) under accelerated conditions.
- Shrinkage/expansion less than one percent over a 12 month period.

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APPENDIX

Literature Review of Fly Ash and Blast Furnace Slag Based Geopolymer Cement Mortars and Concretes Using Alkaline Activator Solutions

This appendix contains a review of available literature regarding the development and inherent properties of alkaline activated geopolymer mortars and cements using commercial fly ash, blast furnace slag and metakaolin as the pozzolanic binder material.

The review is organized by the following categories:

OVERALL GEOPOLYMER ANALYSIS

Skvara, Frantisek, Dolezal, Josef, Svoboda, Pavel, Kopecky, Lubomir, Pawlasova, Simona, Lucuk, Martin, Dvoracek, Kamil, Beksa, Martin, Myskova, Lenka, Sulc, Rostislav, "Concrete Based on Fly Ash Geopolymers",
http://www.vscht.cz/sil/pojiva/Poster_1.62_CD.pdf

The intent of this research is to investigate several definitive properties of fly ash-based geopolymer concretes. Fly ash with a surface fineness of 210 to 300 m^2/kg was obtained from power local power plants in Czechoslovakia and used for all test material mixes. Fine and coarse-grained crushed quarry aggregate with grain-sizes ranging from 0mm to 16mm were utilized. The activating agent was comprised of a SiO_2-to-NaO_2 ratio (M_s modulus) of 1 to 1.6 and alkalinity concentration (Na_2O) of 6-10 percent (per fly ash weight). Some mixes contained limestone, gypsum, and/or pelletized blast-oven slag. Both mortar and aggregate concrete fly ash-based geopolymer materials were created for testing.

Samples were subject to the following test regimes: freeze/thaw (per CSN 72 2452); compressive strength; tensile strength under bending; corrosion resistance and high heat resistance. The chemical composition, porosity and aggregate bonding interface of the geopolymer samples were also analyzed.

It was found that the geopolymer specimens possess excellent frost resistance. After 150 freeze cycles there were no visible defects or degradation present and the compressive strength fell to approximately 70 percent of the non-frozen control group after 28 days.

Mortar samples were subjected to NaCl solution for up to 720 days without damage. The compressive strength of the samples continually increased over time and reached a maximum value of 70 MPa. Virtually no corrosion products could be found after two (2) years in solution and, more importantly, there was an absence of ettringite ($C_6AS_3H_{32}$) and Friedel salt ($C_4 AClH_{11}$) which can eventually cause body disintegration of cement-based concrete from crystallization stresses.

It was noted that samples tested at high temperature (150 to 1100 °C) began losing strength at 250 °C and the lowest values recorded (-40 percent) occurred in the range of 600 to 700 °C. However, no shrinkage due to hydration was noticed and the ratio of compressive-to-tensile strength under bending varies in the range of 10.0:5.5, as related to cement-based concrete at a ratio of 10:1.

High magnification of resulting fractures revealed up to 50 percent porosity as closed spherical pores resulting from dissolution of original fly ash particles and air entrainment during preparation. It is noted that the geopolymer porosity is influenced by the water coefficient value (H_2O-to-fly ash ratio). Furthermore, the samples produced with a mixture of fly ash and blast-oven slag were found to have a lower porosity ranging from 2-10 percent with compressive strengths reaching 160 MPa.

Finally, the investigation of the aggregate-resin interface at high magnification revealed that no porous transition zone was present in the geopolymer specimens, as is generally found within a 20 to 100 µm distances from aggregate surfaces in standard Portland cement mixes.

Vijaya Rangan, B., "Fly Ash-Based Geopolymer Concrete", available at:
http://www.yourbuilding.org/display/yb/Fly+Ash-Based+Geopolymer+Concrete

This publication addresses fly ash-based geopolymer concrete design methodologies and the factors that influence its fresh and hardened mechanic properties. The testing regime was based upon both short and long-term evaluations and conducted using reinforced geopolymer specimens on a large-scale basis.

Testing was conducted upon 100 x 200 mm cylinders that had been both dry and steam cured in 60 °C temperatures from four to 96 hours and first compression tested at 21 days. It was stated that longer curing times resulted in greater compressive strengths. As well, the first 24 hours produced rapid strength gain, while curing beyond 24 hours resulted in a slower strength gain per unit time. It was also noted that dry curing resulted in 15 percent greater compressive strength than steam curing for the same time period.

The aggregate mixture consisted of coarse, SSD aggregates (7-20 mm) and fine sands. Low calcium, class F fly ash was added to the aggregates and mixed for three minutes. A super plasticizer was added to the sodium hydroxide/sodium silicate activator to improve workability. Final testing concluded that the fresh concrete could be worked for up to 120 minutes without affecting the overall compressive strength of the specimen. Furthermore, the alkaline/fly ash ratio for the binder design was recommended to be 0.30-0.45 and the sodium silicate/sodium hydroxide ratio (by mass) was suggested to be 2.5 for best results.

The compressive test results for the elevated cure showed 7-day values of 58 MPa and 45 MPa for the dry cured samples. The steam cured specimens (of elevated temperatures) yielded 56 MPa and 36 MPa, respectively; almost 10 MPa less for mix 2. The ambient cured material produced strength values over 50 MPa. It was noted, however, that batches were mixed during a five month period in which ambient temperatures varied. The following summarizes the recorded temperatures for each batch: May 2005 (18-25 °C), July 2005 (8-18 °C), September 2005 (12-22 °C). The relative humidity for each batch was within the range of 40-60 percent. The material with the greatest recorded compressive strength was molded from the May batch.

Creep and dry shrinkage testing was also performed on 150 x 300 mm cylinders which were both dry- and steam-cured at 60 °C for 24 hours. Testing commenced after one week of cure time and the recorded stress was 40 percent of the compressive strength. Test results illustrated that both cure methods yield similar results. Little shrinkage was observed in the geopolymer specimens after a one year time period. The measured value for geopolymer was 100 micro strains, as compared to 500-800 micro strains for Portland cement concrete. One year creep coefficients were calculated at 0.6-0.7 for specimens possessing compressive strength values between 40 MPa and 57 MPa. It was noted that these values are only 50 percent of the recommended coefficients for Portland cement concrete (per Australian Standard AS3600).

Testing regimes for chemical resistance to sulfates and sulfuric acids were also conducted. Geopolymer specimens were immersed in a 5 percent sodium sulfate bath for up to one year. Factors evaluated were mass and length change and variances in compressive strength characteristics. Other samples were placed into sulfuric acid solutions of varying concentrations: 0.5 percent, 1 percent, and 2 percent (by volume). Factors investigated here were based upon mass losses and changes in overall compressive strength. It was reported

that specimens subjected to the sulfate immersion exemplified excellent resistance to the chemical. Visual observation at one year of exposure reflected no sign of erosion or cracking of the specimens. As well, no changes in mass or compressive characteristics were noticed and the change in overall length was less than 0.015 percent.

The sulfuric acid tests revealed slight erosion to the specimen surface and it was noted that the degradation is increased with increased acid concentrations. Maximum mass loss was reported to be 3 percent after one year, which was stated to be far less than that of similar Portland cement specimens. Compressive strength values were also compromised by the acid bath. As with the degradation, the compressive limits were affected by increases in acid solution concentration.

Finally, the geopolymer material was tested for practical applications by creating and loading column and beam specimens. The test parameters investigated were longitudinal reinforcement ratios, load eccentricity values, and compressive strength. Additional information regarding these tests is defined in detail within the publication body.

McDonald, Mike and LaRosa Thompson, Judy, "Sodium Silicate: A Binder for the 21st Century, *The PQ Corporation, Industrial Chemicals Division,* http://www.pqcorp.com/technicalservice/..%5Cliterature%5Cbinder.pdf.

The effectiveness of soluble silicates used as cementitious binders for agglomerated materials was investigated and discussed. The manufacturing process of these silicate products was described and it was stated that they may represent several types of binder scenarios. The most important property of silicates was said to be it weight ratio of SiO2 to Na_2O, with the value of 3.2 being the most widely adopted ratio providing for the necessary polymerization reactions to occur.

Four chemical phases were stated to exist in consecutive order during silicate reaction with agglomerated materials: hydration/dehydration, gelation, precipitation, and surface charge modification. During hydration, a glassy film is created as water is removed from the liquid silicate, leaving it increasingly more viscous over time, but additional heat is required for full hydrate evacuation and proper curing of the hardened product. Polymerization occurs within the fresh paste as the pH level falls below 10.7 and silicates begin to form crosslinks with the existing pozzolans. It was noted that while the bonds of polymerization are not as strong as those created through dehydration, they boast increased water resistance once formed. Precipitation of formed metal silicates occurs as available multivalent cations (Ca^+, Mg^{+2}, Zn^{+2}, Cu^{+2}, Fe^{+3}) react with the added silicates to form solids and drop out of solution as a chemical binder. Pozzolans such as commercial fly ash, blast furnace slag and cement kiln dust contain many of these required elements needed for precipitation and offer an economic and environmentally safe alternative to the energy intensive manufacture of Portland cement. It was found that unlike other available materials, pozzolans require the introduction of heat and/or chemicals to activate the binder solution and allow for crucial crystalline formations. As well, they tend to set slower (allowing for increased reaction degrees) and they are less susceptible to foreign substances in the matrix. For pozzolan activation, a silicate ratio of 2.0 is recommended.

Khale, Divya, Chaudhary, Rubina, "Mechanism of Geopolymerization and Factors Influencing Its Development: A Review", *Journal of Materials Science 42,* **pp.729-746, 2007.**

This paper discusses the fundamentals of geopolymerization and the empirical evidence that supports its development. It investigates chemical reactions within the matrix, source materials used to induce polycondensation, alkali concentration, curing temperatures and times, water/solid ratios and pH balance.

Geopolymers are polymeric structures of the order Al-O-Si and possess great mechanical strength as a result of alkali-activated polycondensation and pozzolanic reactions within the formed matrix. The rate of these reactions and the mechanical properties of the hardened material are effected by several factors.

High concentrations of alkalis are required to begin chemically interacting with the added pozzolanas. Activating agents such as NaOH, Na_2SO_4, waterglass and KOH are common additives to the pozzolanic substances. Blast furnace slag or commercially available, class F fly ash materials are widely used as the base ingredient. Kaolin is often heated and converted into metakaoline at temperatures between 600-900 °C for use in geopolymer pastes in lieu of traditional fly ash. To improve workability of the resulting paste, superplasticizers are often added, increasing the density and final strength of the mix.

Curing temperature and curing time both increase unconfined compressive strength. Longer curing times result in increased compressive strength values; however, periods beyond 48 hours produce negligible strength increases. Temperature regulation in the 2-5 hour cure period is critical to potential strength development. It was stated that curing temperatures in the range of 30-90 °C are required for adequate chemical reaction.

Overall strength of the geopolymer can also be affected by ingredient ratios and pH levels of the activating solution. Tests concludes that increased water-to-solid ratio decreases strength, while high ratios of Si:Al or Na:Al increase the geopolymer mechanics. Empirical data has shown that a pH level of the activating paste greater than 13 (5-10 M alkali solution) promotes increased reactions and increased strength.

Furthermore, geopolymer cement differs greatly from PCC as related to shrinkage and creep. It has been shown that characteristics regarding Poisson's Ratio, Young's modulus and tensile strength are similar, while geopolymer cement bears little to none of the dry shrinkage and creep characteristics of Portland cement. As well, geopolymer cement has been tested from an environmental perspective and it retains 90 percent of heavy metals within its hardened matrix. It was concluded that geopolymer cement products are cost effective and environmentally sensitive.

Duxson, P., Fernandez-Jimenez, A., Provis, J.L., Lukey, G.C., Palomo, A., van Deventer, J.S.J., "Geopolymer Technology: The Current State of the Art", *J Mater Sci,* **DOI 10.1007/s10853-006-0637-z**

This publication reviews the logistics of geopolymer cement and the technology derived to develop this new material. It is noted that geopolymer cement bears intriguing characteristics of compressive strength potential, fire resistance, low shrinkage during cure and minimal thermal conductivity. As well, the active ingredients in geopolymer cement are typically commercial by-products and therefore eliminate the energy consumption and CO_2 emission currently required for Portland cement manufacture.

Geopolymer cements are termed for the polymer gel that is formed during polycondensation and the amorphous to crystalline transformation of reaction products within the matrix. This transformation is a result of alkali aluminosilicate dissolution (metakaoline or fly ash) and the precipitation reaction resulting from added hydroxides or silicates in solution. The end product is a constantly re-organizing, coagulated gel formation that eventually cures into a hardened, three-dimensional aluminosilicate structure with physical properties similar to Portland cement. The precipitation rate is affected by alkaline concentration, curing temperature, pH of the solution and chemical ratios of the paste mix; increasing temperature during cure and maintaining a high pH level generally increase the reaction rate and overall compressive strength of the hardened geopolymer cement.

It is noted that geopolymer cement boasts several inherent properties potentially beneficial to the commercial industry and apart from those seen in Portland cement, including acid and fire resistance, high adherence to aggregates and a lack of dry shrinkage. It produces no carbon dioxide emission and is expected to provide a cost savings of 10-30 percent over conventional Portland cement concrete. Based upon these properties, it is stated that geopolymer cement concretes have a high potential for future use in global development.

Pacheco-Torgal, F et al, "Alkali-Activated Binders: A Review", *Constr Build Mater (***2007),
doi: 10.1016/j.conbuildmat.2007.10.015.**
This paper reviews current technologies and historical backgrounds of alkali-activated (geopolymer) cement binders and analyzes the reaction mechanisms inherent to these materials. It is known that ordinary PCC has for years shown inadequate properties of acid resistance, durability and requires a great deal of energy and CO_2 emission for general production. Geopolymers, or alkali-activated cements, show promise to remedy the degradation issues seen in Portland cement today. Thus, alkali-activated systems pose less threat to the environment and could offer a lasting alternative to current cement design.

It was reported that while development of alkali-activated binders played an important role in the 1940's, the existence of zeolite-based mortars date back to 7000 B.C. in the valley of the Jordan River. Chemical and mineralogical studies have also shown that the pyramids of Egypt were constructed not of natural stone block, but instead of a mixture of limestone sand, calcium hydroxide, water and sodium carbonate similar to the composition of present day geopolymers.

Pacheco-Torgal, Fernando, Castro-Gomes, Joao, Jalali, Said, "Alkali-Activated Binders: A Review. Part 2. About Materials and Binders Manufacture" *Constr Build Mater* **(2007), doi:10.1016/j.conbuildmat.2007.03.019**
This paper is a conclusion of the analysis presented in Part 1 and further investigates the finite properties of alkali-activated cement, including activating chemical agents, applicable additives, curing methods and proper mixing techniques.

It is stated that in theory, all siliceous and aluminum-based materials can be alkali-activated and combined with choice aggregates to produce polymerized concrete. The majority of pozzolans currently tested as suitable binder materials are in the categories of metakaolins, kaolinitic clays, blast furnace slags and industrial by-product fly ashes. The alkali-activated reaction depends upon the amorphous content of silica and aluminum in the selected pozzolan.

To achieve high strength and lasting durability of the formed cement, it is suggested that the alkaline activators be utilized in the following range of molarity ratios: (SiO_2/Na_2O=1.85; SiO_2/Al_2O_3=3.5-4.5; Na_2O/SiO_2=0.2-0.48; Na_2O/Al_2O_3=0.8-1.6; H_2O/Na_2O=10.0-25.0). However, optimum ratios were reported as Na_2O/SiO_2=0.25, H_2O/Na_2O=10.0, and SiO_2/Al_2O_3=3.3; a high water to sodium oxide ratio (H_2O/Na_2O=25.0) yielded unacceptable mechanical strength values. Activating agents are generally varying concentrations of sodium or potassium hydroxides (NaOH, KOH) and it was generally noticed that an increase of molarity ratio resulted in an increase of final mechanical strength up to a certain level. Increased concentrations above the optimum can actually lower the resulting strength value; each activator should be treated differently and according to empirical evidence.

Additional factors directly affecting final cement properties were curing time, curing temperature, concentration of the activator and finally the Blaine Fineness of the pozzolan material. As with alkaline concentrations, curing temperatures are relative to the mix design and proportionality. Studies show that increased temperature of specimens activated with NaOH and waterglass cause a reduction in strength, whereas samples produced without waterglass, a strength increase is noticed.

It is concluded that the most applicable activators remain to be hydroxides and soluble silica and that the use of calcium hydroxide often leads to improved strength characteristics. Regardless, it was conceded that little is still known about geopolymers and their products as a function of alkaline reactivity and time. Further research of alkali-activation and aluminosilicate minerals is suggested.

MECHANICAL PROPERTIES

Lee, W.K.W., and Van Deventer, J.S.J., "The Interface Between Natural Siliceous Aggregates and Geopolymers", *Cement and Concrete Research 34*, **pp. 195-206, 2004.**
    This paper describes research on the microstructure and bonding strength of the interface between natural siliceous aggregates and fly ash geoploymers. Tests performed with geopolymeric gel binders of varying degrees of soluble silicate dosages for both mortars and concrete mixes. High levels of soluble silicates greatly increased interface bonding between the binder and the aggregate surface. Soluble silicates effectively reduced alkali saturation of the concrete pore solution. Interfacial bonding between aggregate and geopolymeric binders is critical in determining the effective mechanical strengths of geopolymer mortars and concretes.

Sumajouw, D.M.J., Hardjito, D., Wallah, S.E., and Rangan, B.V., "Fly Ash-Based Geopolymer Concrete: Study of Slender Reinforced Columns", *Journal of Materials Science*, **pp.42:3124-3130, 2007.**
    This study focused on the use of geopolymer concrete in structurally reinforced columns. A low calcium fly ash mixed with sodium hydroxide (NaOH) and a sodium silicate solution formed the applied binder paste. The geopolymer material was formed into twelve longitudinally-reinforced columns of 175 mm^2 by 1500-mm-long each. The authors produced two series of geopolymer material mixes to achieve an average compressive strength of 40 MPa and 60 MPa, respectively. Steam at 60 °C cured all samples for 24 hours prior to testing. Post-test results reveal geopolymer mechanics similar to the design provisions reflected in the Australian Standard AS 3600 and the ACI Building Code ACI 318-02 for standard Portland cement concrete structures. The authors noted that this research provides

evidence that design revisions contained in current standards and codes can be used to design and manufacture environmentally agreeable, fly ash-based geopolymer concrete columns.

Sofi, M., van Deventer, J.S.J., Mendis, P.A., Lukey, G.C., "Engineering Properties of Inorganic Polymer Concretes (IPC's)", *Cement and Concrete Research 37***, pp. 251-257, 2007.**

Structural comparisons between inorganic polymer concretes (IPC's) and PCC-based concrete were studied. Few published studies on the engineering properties of IPC's exist; therefore, the following IPC tests were conducted: compressive strength, splitting tensile strength, flexural strength, static chord modulus of elasticity and Poisson's Ratio. For IPC densities similar to Portland cement concretes, the average compressive strengths of the IPC mixes were close to the design strength of 52.4-MPa. The splitting tensile and flexural strength IPC models compared to those of PCC. The static chord modulus and Poison's Ratio evaluations yielded results similar to high-strength PCC.

Hardjito, Djwantoro, Wallah, Steenie E., Sumajouw, Dody M.J., and Rangan B.V., "The Stress-Strain Behavior of Fly Ash-Based Geopolymer Concrete", *Developments in Mechanics of Structures and Materials***, 2005 Taylor & Francis Group, London, ISBN 90 5809 659 9**

This publication investigates the stress-strain behavior of geopolymer concrete using low calcium (class F) fly ash-based material. The compressive strengths of the test material were in the 40-80 MPa range. The testing specimens were 100 x 200 mm (compressive testing) and 150 x 300 mm cylinders (tensile split testing) and results were compared with stress-strain models for Portland cement concrete. The geopolymer resin mix was comprised of fly ash with a specific surface area of $1.94 m^2/mm^3$, a sodium silicate solution and sodium hydroxide (pellet or flakes) dissolved in water. Sulphonated-naphthanlene superplasticiser was added to improve the workability. The aggregate mix consisted of 10 mm and 7 mm coarse granite and fine sand with a combined fineness modulus of 4.5. Five specimen molds were cast for each test variable and oven cured for 24 hours, followed by six hours at ambient temperature. Test procedures were performed per the Australian Standards for concrete testing. Stress-strain curve were obtained and compared to Portland cement concrete curve under similar conditions. Tensile splitting tests were performed per AS 1012.10-2000 (2000) and yielded similar results to Portland cement concrete. In conclusion, there are many mechanical similarities between the fly ash-based geopolymer concrete and Portland cement concrete. Geopolymer fly ash-based concrete may be applicable to the provisions and codes currently written for Portland cement concrete.

Fernandez-Jimenez, A., I., Palomo, A., Lapez-Hombrados, C., "Engineering Properties of Alkali—Activated Fly Ash Concrete", *ACI Materials Journal***, available at:** http://findarticles.com/p/articles/mi_qa5360/is_200603/ai_n21395768**, Mar/Apr 2006.**

This research focuses upon the mechanical properties of alkali-activated fly ash concrete. Experimental testing was conducted to determine the following: compressive and bending strengths, modulus of elasticity, pull-out bond strength and mass shrinkage. Specimens of ordinary Portland cement concrete were also tested as a control group.

The compression testing was performed on 15 cm^3 cubes and the bending strength testing on 15 x 10 x 70 cm prisms. The modulus of elasticity specimens were constructed as 15 cm^2 x 20 cm cylinders per Spanish standard UNE 83316. Pull out tests were performed on 20 cm^2 cubes and the mass shrinkage tests on 2.5 cm^2 x 23 cm prisms.

Two separate designs of alkaline activators were prepared: 'Solution N' (8 M NaOH solution) and 'Solution W' (85 percent 12.5 M NaOH solution, 15 percent sodium silicate solution). Each paste received coarse siliceous aggregate (6-12 mm) and fine river sand (0-5 mm) in a 1.26:1 ratio. The PCC design (Type HA3) utilized the same aggregate dosage, but differed in their water/cement ratios and a lignosulphonate-based admixture was added at 0.84 percent (by binder weight).

Curing for the PCC specimens were conducted at different temperatures: 20 hours at 22 °C and 20 hours at 40 °C. The AAFA mortars were cured using the same criteria: 20 hours at 85 °C and then stored in the lab at 21 °C and 50 percent relative humidity (RH). For all specimens, shrinkage measurements were observed at one, three, seven, 14, and 28 days from time of initial cure end.

Mechanical testing of the alkali-activated specimens (N/W) yielded values of 45 MPa after 24 hours of cure time. It was found that the compressive strength continued to increase thereafter, but at a slower rate than the first 24 hour period. It was also noted that the addition of soluble silica increased the strength, yet decreased the workability of the material mix. Flexural testing results indicated an initial strength acquisition with gradual strengthening over time.

The modulus of elasticity testing was performed with equipment conforming to Spanish standard UNE 83304 which is capable of applying and maintaining simultaneous rate and interval loading. Results confirmed that the Portland cement-free specimens achieved lower elasticity values than the Portland cement control group.

Pull out tests were performed by embedding steel bar of diameters 8 and 16 mm by 70 cm in length into the center of the 20 cm^3 concrete specimen. Both ends were plastic coated to prevent bonding outside of the intended length. A 156 kN hydraulic jack was used at a rate of 72 N/s until failure occurred. Testing observation revealed that the bonding within the AAFA materials caused the 8 mm bars to break prior to bond sheer. Conversely, the bars embedded in the PCC material slipped prior to bar damage. It is noted that the Solution 'W' reached an ultimate stress of 12.5 MPa, while Solution 'N' achieved 17 MPa; each higher than the 9.7 N/mm beam test requirement per the Spanish concrete code (EHE).

Finally, shrinkage analysis for the AAFA materials (both N and W) showed less than 0.025 percent reduction after 90 days, versus 0.09 percent for the PCC samples. It was noted that these results illustrate the dimensional stability of alkali-activated fly ash concretes.

Fernandez-Jimenez, A., Palomo, J.G., Puertas, F., "Alkali-Activated Slag Mortars: Mechanical Strength Behavior", *Cement and Concrete Research 29***, pp. 1313-1321, 1999.**
This research considers factors such as slag specific surfaces, activator concentrations and curing temperatures and their effect on the mechanics of alkali-activated slag cement mortars. Specimens were developed using Na_2SO_3 + NaOH as the activator chemical base and then evaluated at specified intervals from three to 180 days. Each factor was rated from greatest to least influence on the resulting strength value through utilization of statistical analysis via STATGRAPHICS Plus computer software. Details of the analysis and final model equations derived from the flexural and compressive behavior data are presented in the final report.

The mortar used in testing was prepared in accordance with the Spanish standard UNE-80-101-88 with Spanish blast furnace slag from local industry. Specimen prisms were constructed using a 2:1 aggregate/slag ratio and an alkaline/slag ratio of 0.51 for the 450 m^2/kg slag material and 0.61 for the 900 m^2/kg batch. Curing time was 20 hours at two differing temperatures: 25 °C and 45 °C. Compressive and flexural testing regimes were conducted at three, seven, 28, 90 and 180 days.

A combination of test data and statistical analysis revealed that the slag specific surface used in the batch mix is least relevant to the resultant mechanical properties of the geopolymer. The second most relevant factor was found to be the curing temperature, followed immediately by the activator concentration. Thus, the factor determined to hold the greatest significance as related to mechanical strength was the nature of the alkaline activator. The highest mechanical strengths recorded during this research (6-8 MPa for flexural and 40-60 MPa for compressive) resulted from an activator mix of Na_2SO_3, $NAOH$ and H_2O.

Songpiriyakij, S., "Alkali-Activated Fly Ash Concrete", *Mongkut's Institute of Technology North Bangkok, Thailand***, email:** ssy@kmitnb.ac.th

This research investigates alkali-activated fly ash concrete using seven different ratios of sodium hydroxide (NaOH) and sodium silicate (Na_2SO_3) as the binding activators. The geopolymer material was diluted with water until the slump reached approximately 200 mm. Cubed specimens (100 mm^3) were molded and cured at two separate temperatures: one mix at 60 °C for 24 hours and the other at ambient (25 °C).

All mix designs consisted of class F fly ash with a specific surface area of 2120 cm^2/g and saturated surface dry river sand/limestone of 3/8 inch maximum size. The differences in each mix was in the amount of fly ash added, the Na_2O:SiO_2 ratio and various chemical ratios. Compressive strength testing of mixes 1-3 revealed values unsuitable for structural concrete, however, mixes 4-7 yielded much higher results. Mixes 4-7 were designed using a higher fly ash percentage and a greater sodium oxide to silicate ratio. It was noted that as the Na_2O/SiO_2 ratio increases, the compressive strength of the resulting concrete specimen increases. However, it was shown that each chemical activator maintained an optimum ratio; increasing the ratio above the optimum level resulted in a decline of compressive strength.

BINDER CHEMICAL INTERACTIONS

Lee, W.K.W., van Deventer, J.S.J., "Chemical Interactions Between Siliceous Aggregates and Low-Ca Alkali-Activated Cements", *Cement and Concrete Research 37***, pp.844-855, 2007.**

Chemical interaction between natural siliceous aggregates and low-Ca alkali-activated, geopolymer cement was investigated. Various aluminosilicate materials (kaolinite and albite) were leached in alkaline solutions with or without soluble silicates and aluminum enriched aluminosilicate formed on the surface level, facilitating soluble silicate depositions and formations of a dense aluminosilicate gel interfacial layer. The gel can be used to bind various mineral aggregates (sand/natural rock) producing mortars and concretes. The deposited aluminosilicate (Si/Al ratio of 3), resembles the real interface between natural siliceous aggregate (basalt, siltstone) and a low-Ca alkali-activated cement. The cement was activated by high solution alkalinity ($[OH^-]_0$=10M) and soluble silicates ($[SiO_2]_0$=2.5M). Without soluble silicates, no deposited aluminosilicate interface was observed. It was concluded that both high concentrations of solution alkalinities and soluble silicates are

essential for the formation of a strong interface between siliceous aggregates and low-Ca alkali-activated cements.

Xie, Zhaohui, Xi, Yunping, "Hardening Mechanisms of an Alkaline-Activated Class F Fly Ash", *Cement and Concrete Research 31,* **pp. 1245-1249, 2001.**

This paper addresses the mechanisms by which fly ash-based geopolymer cements obtain their hardened properties. Low calcium, class F fly ash paste was formed by employing water glass (1.64 modulus) as the activating agent in a fly ash/water glass/water ratio of 26:15:1. XRD and SEM-EDS analysis was conducted to closely inspect the paste infrastructure for evident hardening mechanisms. Specimen molds were cast and cured for 24 hours at 60 °C prior to testing. The fly ash product used was found to be high in reactive oxide content, thus was expected to react aggressively with the alkaline water glass and produce a cement matrix of high strength in a short time period.

Reaction products formed were found to be of type Na_2O-Al_2O_3-SiO_2 in an amorphous state or low-order crystalline structure. This product worked together with the hydrolysis-formed silica gel to harden the binder and create strength within the matrix. The decrease of water glass modulus to 1.0 (NaOH addition) produced excessive sodium silicate crystals and thus, resulted in a more dense, higher strength material. It was found that reducing the modulus results in an increase of unreacted fly ash particles within the matrix leading to a higher strength material.

MINERALOGICAL/MICROSTRUCTURAL ANALYSIS

Puertas, F., Fernandez-Jimenez, A., "Mineralogical and Microstructural Characterization of Alkali-Activated Fly Ash/Slag Pastes", *Cement and Concrete Composites 25*, **pp. 287-292, 2003.**

This research focuses upon the microstructural aspects of fly ash and/or slag-activated geopolymer concretes. Testing analysis was carried out using XRD, FTIR, MAS-NMR, and SEM/EDX devices. As well, atomic absorption and ion chromatography were studied in depth. It was reported that two reaction products were realized through this research: a calcium hydrate rich in aluminum and an alkaline aluminosilicate hydrate with three-dimensional structure.

The slag obtained for use was found via XRD to consist mainly of a glassy phase, absent of crystalline phase. The fly ash was analyzed similarly and found to consist of a glass phase, quartz and mullite. Further testing of the slag material confirmed a composition near that of Akermanite and Gehlenite.

Mechanical testing was conducted on 1 x 1 x 6 cm prisms with a fly ash/slag ratio of 1.0. The proprietary activator used was NaOH at a concentration of 10M. Curing was conducted for five hours at two separate temperatures for comparison: 22 °C and 60 °C. Each specimen then remained at ambient temperature with 98 percent relative humidity for seven and 28 days prior to testing. Compressive testing results at seven days cure time were recorded at 30 MPa for each mix design. It was surprisingly revealed that the specimens cured at ambient developed over 60 MPa of compressive strength within a 28 day cure period; higher than the samples cured at 65 °C.

It was discovered that the degree of silicate polymerization varies directly with reaction time; thus, longer cure times allow for greater polymerization and greater overall concrete strength.

Furthermore, this researched revealed that the reaction products formed around the fly ash particles are an amorphous alkaline aluminosilicate hydrate with three dimension structural properties.

Katz, A., "Microscopic Study of Alkali-Activated Fly Ash", *Cement and Concrete Research*, **Vol. 28, No. 2, pp. 197-208, 1998.**

This paper researches fly ash reactivity within an alkaline environment and means by which to improve polymerization methods. The activator used for testing was a strong sodium hydroxide (NaOH) solution of variant concentrations and water/fly ash ratios. The maximum temperature of cure was 90 °C and 4 M NaOH was the highest concentration level utilized.

Testing was completed in three phases which addressed the following effects: NaOH concentration, water/fly ash ratio, curing temperatures. Test specimens consisted of $25mm^3$ molds immersed in 1-4 M NaOH solution baths. Compressive testing for all concentration specimens was conducted on day seven and yielded results proving a direct relationship between alkalinity and compressive strength: the 4 M NaOH solution provided compression values of nearly 6 MPa (at 7 days), while the 1 M solution samples yielded at 0.2 MPa.

SEM analysis was also reviewed for all concentration levels. No fly ash reactions were evident in the 1 M solution, but the higher concentrations (3M NaOH) resulted in surface etching and needle-like crystals had formed. The 4 M solution was observed to have undergone microstructural change, bearing cubic crystalline formations unlike those found in the 3 M solution. It was concluded that the given matrix had become less porous and densification had occurred at the higher concentrations.

Lee, C.Y., Lee H.K., Lee, K.M., "Strength and Microstructural Characteristics of Chemically Activated Fly Ash-Cement Systems", *Cement and Concrete Research 33*, **pp. 425-431, 2003.**

This paper reports the findings of an investigation into the strength and microstructural properties of fly ash systems activated with different alkaline solutions. Thermal gravitation analysis, x-ray diffraction, scanning electron microscopy and mercury intrusion porosimetry were utilized to observed and document the early stages of development within each system.

The materials used included Type I Portland cement and low-calcium fly ash obtained in South Korea. Washed river sand was also incorporated as the fine aggregate in the mortar mix. Activators involved were Na_2SO_4 and K_2SO_4, with a third organic activator, thiethanolamine. Mortars were mixed in a water/cement material ratio of 0.485 and a fine aggregate/cement material ratio of 2.45. The fresh paste and mortar mixes were formed into 10 cm^3 steel molds and allowed to remain for 24 hours before being demolded, and water bath cured for up to 28 days at 20 °C. Compressive testing regimes were conducted at 1, 3, 7 and 28 days and the tested samples were then crushed and immersed in acetone to prevent further hydration and freeze-dried prior to micro-analysis.

Compression analysis at one day of cure revealed greater strengths in the activated pastes than those receiving no alkaline activation. Of all activator solutions evaluated, the potassium-based alkaline (K_2SO_4) was found to be most effective in promoting early strength development and reducing porosity, while those containing triethanolamine maintained the lowest results of compressive strengths. N_2SO_4 was found to efficiently decrease the levels of $Ca(OH)_2$ in the paste mixes and promoted growth of ettringite within seven days of cure, aiding the high strength development observed via XRD analysis.

It was concluded that while the activators employed for this experiment promoted early strength development, the measured strength values at 28 days were comparable to the fly ash/Portland mixes absent of alkaline activators. It was stated that further testing would be required to fully understand the affects related to activation in both early and late stage development.

Williams, P. Jason, Biernacki, Joseph J., Walker, Larry R., Meyer, Harry M., Rawn, Claudia J., Bai, Jianming, "Microanalysis of Alkali-Activated Fly Ash-CH Pastes", *Cement and Concrete Research 32,* **pp. 963-972, 2002.**

This paper analyzes the micro-level hydration effects of utilizing reagent grade calcium hydroxide (CH) in a (class F) fly ash geopolymer paste with sodium hydroxide solution activator. The fly ash was comprised of aluminosilicate glass and silica and the alkaline immersion maintained a 13.2 pH level. The microanalysis was performed using x-ray and a backscattered electron scanning Auger technologies. Immersion observations were held at eight, 14 and 78 days under various temperatures.

The paste was constructed at a 50:50 CH-to-fly ash ratio using 0.2 M NaOH as the activating agent. Rapid curing took place in glass vials that were then broken to release the mold. Specimens were broken for fracture analysis, embedded in epoxy or polished. Final analysis was performed using one of the following methods: thermalgravimetric (TGA), Synchrotron x-ray diffraction, or SEM/EDS microanalysis.

It was found that both CH and fly ash particles developed early stage surface hydrated growth products (including katoite) that were of the C-S-H type. The Ca/Si ratio of 1.4 was less than that of similarly tested Portland cement material. It was rationalized that hydration rates increase with higher levels of CH/fly ash in the initial paste.

Fernandez-Jimenez, A., Palomo, A., Criado, M., "Microstructure Development of Alkali-Activated Fly Ash Cement: A Descriptive Model", *Cement and Concrete Research 35*, **pp. 1204-1209, 2005.**

This research discusses a model generated from the microscopic study of an alkali-activated and heat-cured fly ash based geopolymer sample. The model analyzes the real time activation of spherical fly ash particles through a consecutive step series and has been cross-analyzed with data from XRD, FTIR and MAS-NMR technologies.

The fly ash utilized had a high SiO_2 content and was dissolved with an 8 M NaOH solution in a ratio of 0.35 (NaOH/fly ash). Formed molds were oven-cured at 85 °C for five hours, 24 hours and up to 60 days and then frozen in acetone for testing.

Reactivity versus time of the specimens was reviewed and showed a high percentage of reaction within the first hour of thermal curing; the remaining time curve maintained a normal increasing curve over time. The alkaline-induced reaction product is a compacted aluminosilicate gel which encapsulates the hardening mechanism in the cement matrix. SEM analysis revealed fly ash particle reactions ranging from partial particle disintegration with smaller particles trapped within to no visible signs of reactive degradation at all. High reaction rates greater than 60 percent produce Si/Al ratios in the range of 1.9-2.1 and a dense matrix paste with increased mechanical strengths.

These reactions are stated to be categorized into four discernible stages: nucleation, dissolution, and polymerization and crystal growth. Nucleation is defined as the

aluminosilicate product being dissolved into the alkaline solution. Two sub-phases have been defined during this phase: dissolution and polymerization. The dissolution sub-phase produces specific Si and Al ions from the immersed ash product, but is highly dependent upon the pH level of the host solution. The polymerization sub-phase is shown to enhance precipitation of the suspended molecules and a semi-ordered gel structure begins to appear. The final phase embodies crystal formation and was shown to develop slowly over time as a result of low alkaline/fly ash ratios and depend greatly upon particle distribution and mineral structure of the original fly ash.

Fernandez-Jimenez, A., Palomo, A., "Mid-Infrared Specroscopic Studies of Alkali-Activated Fly Ash Structure", *Micoporous and Mesoporous Materials 86*, **pp. 207-214, 2005.**
This research was conducted to investigate the formations of zeolite precursors in alkali activated fly ash cements using infrared technology. Three separate types of fly ash materials (with varying vitreous and crystalline phases) were obtained for detailed analysis. The samples were mixed and activated with an 8 M NaOH solution and heat cured at 85 °C for set time intervals (2 hours, 5 hours, 8 hours, 20 hours and 7 days). An x-ray diffractometer (XRD) reading and Fourier Transform Infrared Spectrometry (FTIR) were used for micro and mineralogical analysis at each specified interval.

Prior to activation, the ash samples were analyzed using XRD and FTIR to obtain data on the initial material. Immediately after, each ash sample was introduced to a 1 percent HF acid solution to dissolve the vitreous phase of the ash, leaving the crystalline products to remain for a repeat analysis. A second attack was performed using a 1:20 HCl solution to dissolve away all but the unreacted ash particles for determinative reactivity analysis.

XRD spectra detailed reviews were conducted and it was concluded that the reaction product gel material has properties of a zeolite precursor, rich in silicates and aluminum and is of S4R-type order initially. However, the final product was determined to morph into a D6R-type order after full cure time. It was noted that IR spectroscopy is effective in microscopic analysis of alkali-activated fly ash cements.

Fernandez-Jimenez, A., Palomo, A., Sobrados, I., Sanz, J., "The Role Played by the Reactive Alumina Content in the Alkaline Activation of Fly Ashes", *Microporous and Mesoporous Materials 91*, **pp. 111-119, 2006.**
The intent of this research was to better understand the relationship between initial fly ash chemical composition and the mechanical/microstructural properties of the resulting alkali-activated cementitious product. The separate class F fly ash samples (P, L, M) were obtained and activated with an 8 M NaOH solution prior to being stored at 85 °C (98 percent relative humidity) during cure. Cure times before mechanical testing ranged from two hours to seven days. The following technologies were employed for microscopic analysis: XRD, ^{29}Si and ^{27}Al MAS-NMR and SEM/EDX. Mechanical testing for compression and flexural strength was performed on (4 x 4 x 16 cm) prismatic molds with a 2:1 fly ash to quartz sand ratio after curing for 168 hours at 85 °C with greater than 95 percent relative humidity.

An initial reaction analysis was conducted using a 1:20 HCl solution to dissolve all aluminosilicate gels and formed zeolites, allowing a quantitative determination of unreacted fly ash particles. It was noticed that a prolonged curing time increased the degree of reaction in mixes L and P, however no reaction change was measured in mix M after eight hours of cure time.

XRD analysis revealed formations of herschelite and hydroxysodalite crystalline phases during long reaction times. ^{29}Si MAS-NMR spectroscopy of the raw ash used initially produced wide signals indicative of a heterogeneous mix. Spectra peaks were measured between -84 and -103 ppm and were attributed to the various forms of silicon within the ash. Other signals were identified as mullite, cristobalite and quartz. Further analysis of the reacted ash paste identified the early stages of reaction as the most critical for product development. An intense signal representing a tectosilicate rich in aluminum was discovered between two and eight hours of cure time. Final comparison of all reacted ashes tested concluded that seven days of cure at 85 °C produce the most thermodynamically stable compound resulting from the activation process. Additionally, the ^{27}Al MAS-NMR testing revealed a signal shift from tetrahedral aluminum, suggesting that aluminum in the zeolite precursors always remain tetrahedrally aligned.

Mechanical test measurements show that the compressive strengths of the hardened material increases substantially between five and 20 hours of cure time in mixes L and P, while mix M showed no considerable strength gain. The highest recorded compressive value was from mix P at ±80 MPa. Mix L followed behind testing at 72 MPa and mix M failed at a mere 31 MPa, which was determined to be directly related to a rapid consumption of its reactive Al_2O_3 during the first gel formation. Fly ashes containing high levels of reactive SiO_2 and Al_2O_3 in ratios below (2.0) are found to bear increased mechanical and microstructural properties.

It was determined that fly ash activation involves three distinct stages including dissolution, induction and silicon incorporation. During the dissolution stage, the vitreous phase is completely dissolved and no mechanical strength characteristics are witnessed. The induction stage begins a precipitation of gel coated fly ash particles and the consumption of reactive aluminum, forming the initial microstructural framework for the matrix. The silicon incorporation stage transforms the original metastable gel into a Si-rich gel formation reaching 90 percent reactivity within the mix and the mechanical strength of the system increases considerably.

It was concluded that the availability of Al and Si within the original ash is imperative to proper microstructure formation and an ultimately high strength gain. Variables including activator concentration, curing temperature and time of cure greatly influence gel formation and overall material properties.

Arjunan, P., Silsbee, M.R., Roy, D.M., "Chemical Activation of Low Calcium Fly Ash Part II: Effect of Mineralogical Composition on Alkali Activation", *2001 International Ash Utilization Symposium, Center for Applied Energy Research, University of Kentucky, Paper #106*, **available at:** www.flyash.info

This study addresses the mechanical and chemical variables present within a low calcium fly ash paste activated with a low concentration of sodium hydroxide solution. Observation techniques and mechanical testing of the hardened subjects include x-ray diffraction analysis, SEM and hydration calorimetry and compressive strength measurements.

Testing specimens were created using the following design parameters: (UT) untreated fly ash mixed with PCC; (WT) fly ash mixed with PCC and slurried with water; (Q185CtLo) fly ash treated with 0.08 N NaOH solution and mixed with PCC; (Q185CtLoD) fly ash treated with dry 0.08 N NaOH and mixed with PCC; (Q185CtHi) fly ash treated with 0.8 N NaOH

solution and mixed with PCC; (Q185CtHiD) fly ash treated with dry 0.8 N NaOH and mixed with PCC; 100 percent PCC as a control group. All mixtures were then subject to mixing with Type I PCC at an 80:20 ratio and a 0.30 water content.

Hydration heat was recorded over a 24 hour period using a calorimeter device. X-ray analysis was performed both on the initial ash material prior to activation and the slurries, alike. SEM analysis was conducted on initial fly ash material and slurry specimens activated with 0.08 N NaOH for two hours. Specimens were coated with a thin layer of gold to enhance electric conductivity and examined using dual stage scanning microscopy for all measurements.

It was found that the initial fly ash possessed quartz and major crystalline phases, but the amorphous content varied slightly. Quantitative analysis was performed through phosphoric dissolution. Compressive strength results from one and 28 day cures show a greater performance from the (CtLo) specimen than other specimens of equivalent curing times. The (CtHi) specimen produced low compressive values indicating insufficient ash activation and the specimens created using 0.8 N NaOH displayed poor particle distribution.

It was found that drying mixing produced lower mechanical strength than wet, slurry mixing. This was rationalized as increased corrosion of fly ash particles in the wet mix, thus allowing additional pozzolanic reactions to occur faster.

Additional testing to optimize activator concentrations was performed using varying normalities of NaOH from 0.05 N to 0.25 N solutions. One and 28 day mechanical testing of the hardened specimens revealed compressive strengths equal to or greater than that of the 100 percent PCC control group. A 5-10 percent increase was observed for normalities below 0.1 N, but 28 day strength values declined for specimens activated at 0.1 N, or above.

It was concluded that low concentrations of NaOH are acceptable for fly ash activations and the mineralogical content of the initial low calcium ash does not affect the activation intensity. For fly ash mixtures with PCC, initial activation with NaOH is required for early strength gain. Finally, it was stated that 0.05 N to 0.1 N concentrations of NaOH result in an optimized activation for low calcium fly ash materials.

Fernandez-Jimenez, A., Palomo, A., "Composition and Microstructure of Alkali Activated Fly Ash Binder: Effect of the Activator", *Cement and Concrete Research 35*, **pp. 1984-1992, 2005.**

This research defines the relationship between the mineralogical and microstructural properties of alkali activated fly ash cement materials. Several activators were employed in this study and it was found that regardless of type used, the main reaction product formed is an aluminosilicate gel of low-order, crystalline structure. However, the Si/Al and Na/Al ratios are directly affected by the type of activator used and thus, mechanical strength properties are affected accordingly.

The fly ash used was a Spanish Type F obtained from anthracite and soft coal materials and contained particle sizes smaller than 10µm in diameter. Three different activators were used to create the pozzolanic pastes: NaOH, sodium silicate and anhydrous sodium carbonate. Prismatic molds of the resulting aggregate pastes (aggregate/fly ash ratio of 2:1) were formed for mechanical testing (per Spanish standard UNE-80-101-88) and allowed to cure at 85 °C for 20 hours prior to compressive and flexural analysis.

It was found that the presence of Na_2O directly increases the resulting mechanical strength of the matrix with compressive values reaching 70.4 MPa. In addition, soluble silica bears the the same positive affect and strength values of up to 90 MPa have been recorded after 20 hours of cure time. It was noted however, that in such cases, the SiO_2/Na_2O ratio and the water to binder (w/b) ratio are critical variables. Testing reports show that the highest compressive value during this experiment resulted from a solution to fly ash ratio of 0.4 and a SiO_2/Na_2O ratio of 0.118; lower than this produces a reduction in long term mechanical performance. Finally, the specimens activated with sodium carbonate $[Na_2(CO_3)]$ are shown to maintain lower strengths than those without the presence of a carbonate substance.

Micro analysis was performed using XRD, FTIR and SEM/EDX technologies and it was found that the OH^- ions behave as a reaction catalyst in the paste, allowing the free Na^+ cation to begin the structural building process. A tetrahedral zeolitic gel is formed and heterogeneously distributed throughout the matrix providing available residency for hydrated sodium ions.

Fernandez-Jimenez, A., Palomo, A., Criado, M., "Microstructure Development of Alkali Activated Fly Ash Cement: A Descriptive Model", *Cement and Concrete Research 35***, pp. 1204-1209, 2005.**

The purpose for this paper was to empirically establish a microstructural development model for fly ash activated geopolymer cements. The experiment was conducted using a class F fly ash material with a SiO_2 content of greater than 50 percent. An 8 M NaOH solution was mixed with the ash at a ratio of 0.35 (solution/ash) and allowed to cure in plastic molds at 85 °C for up to 60 days. Specimens were then removed from the oven environment and frozen in acetone for further testing which included acid dissolution and SEM/EDS analysis.

As with previous studies conducted, the early stage reaction degree was found to increase rapidly with a slow progression of reaction thereafter. A percentage of the spherical ash particles were immediately deteriorated, revealing additional, smaller particles within, allowing for further reaction progress. The degree of reaction was measured at almost 50% within five (5) hours of thermal cure. From five to 20 hours of cure time, the reaction rate slowed and the degree at 20 hours was shown to be at 50 percent. As well, the Si content of the formed gel was greater then, than at the five hour point. At 60 days of cure, the reaction degree had been recorded at almost 70 percent with a compacted matrix of Si/Al ratio in the range of 1.9 to 2.1.

It was noted from conclusions that class F fly ash is suitable for alkali-activation; however, several key factors must be addressed during the activation process. Among those are particle size and distribution of the initial ash, relative silica content and the vitreous phase content of the reacting ash material. It was commented that alkali-activation represents specific stages of development. Nucleation was dubbed for the process by which the ash dissolves into the alkaline solution and begins its transformation to an aluminosilicate gel. Two substages are defined within nucleation: dissolution and polymerization. Dissolution involves the breakdown of present aluminosilicates and the formation of ionic species within solution, resulting in rapid heat generation and is directly related to the pH of the system. Polymerization is a process of precipitation of larger molecules where a short order structure may be observed. As reactions increase, an evolution to a Si-rich environment takes place and the development of $Q_4(nAl)$ exists. The second major stage of development is crystalline growth which is dependent upon liquid availability within the matrix. It is noted that quick

precipitation and subsequent hardening of the material can affect crystallinity and inhibit the growth of a well-organized zeolitic structure.

Puertas, F., Fernandez-Jimenez, A., "Mineralogical and Microstructural Characterization of Alkali-Activated Fly Ash/Slag Pastes", *Cement and Concrete Composites 25*, **pp. 287-292, 2003.**

This paper characterizes mineralogical, microstructural and mechanical properties of fly ash/slag cements activated by alkaline solutions and cured at various temperatures. Micro observation was conducted using XRD, FTIR, MAS-NMR, atomic absorption and ion chromatography and SEM/EDX technologies. Detailed analysis of the hardened material included flexural and compressive strength testing, mineralogical examination and characterization via XRD and FTIR spectroscopy. Microstructural analysis was achieved through the use of SEM/EDX and ^{27}Al and ^{29}Si MAS-NMR. Additionally, HCl acid testing on both initial ash samples and activated specimens was conducted to evaluate quantities of residual fly ash particles and predict the actual reaction degree from activation.

The paste was created by activating the 1:1 fly ash/slag mixture with a 10 M NaOH solution in a liquid to solid ratio of 0.35 (by weight). Prism molds of dimension (1 x 1 x 6 cm) were poured and allowed to cure for five hours at two different temperatures: 22 °C and 65 °C. Specimens were then removed from the elevated temperature environment and placed in ambient conditions (98 percent relative humidity) for up to 28 days; testing commenced at seven and 28 days.

Compressive strength results for both specimen types were approximately 30MPa at the seven day testing mark, while those tested at 28 days yielded greater values for the specimens cured at 22 °C (63.5 MPa) than those at 65 °C (53.3 MPa). For the dissolution acid test, it was found that longer reaction times within the matrix yields decreased Insoluble Residue (IR) amounts. Where acid testing of the raw ash mixture prior to activation resulted in a 38.9 percent IR, specimens were allowed to cure for the seven and 28 day cycles produced less IR (23 percent and 30 percent, respectively). This supports the assumption that once activated, fly ash progressively reacts with and polymerizes within the alkaline solution as time passes. While it had been shown through SEM and NMR diagnosis that the main reaction products from the fly ash/slag reacted pastes are calcium and aluminosilicate hydrates, separate analysis of raw slag and ash substances shows that two different, yet distinct reaction products exist in these substances during their reaction evolution. They were found to be an amorphous calcium silicate hydrates and a zeolitic gel compounds encompassing the slag/fly ash particles; the signal intensities of each were found to increase with time.

CHEMICAL RESISTANCE

Sumajouw, D.M.J., Hardjito, D., Wallah, S.E., and Rangan, B.V., "Geopolymer Concrete for a Sustainable Future"*, Presented: Green Processing Conference, Fremantle, WA.*, 10-12 May 2004.

The research presented in this paper includes compressive strength testing, creep and drying shrinkage and sulfate resistance of a fly ash-based geopolymer concrete consisting of 20, 14 and 7 mm aggregates and fine sand with an overall fineness modulus of 5.0. A high range water reducer superplasticizer was utilized to improve workability of the material. The testing was performed on the following specimens: 100 x 200 mm cylinders (compressive strength), 75 x 75 x 285 mm prisms (change in length), and 150 x 300 mm cylinders (creep

and shrinkage). Higher concentrations of NaOH, higher ratios of sodium silicate-to-NaOH, and a curing temperature of up to 60 °C result in higher compressive strength of the test specimens. Curing times greater than 48 hours produced no additional increase in compressive strength. The creep factor was observed at 0.3 after six weeks and the drying shrinkage strains were insignificant. It was concluded that geopolymer concrete properties were unaffected by the controlled sulfate immersion and resist intrusion of chloride and sulfate agents.

Song, Xiujiang, "Development and Performance of Class F Fly Ash Based Geopolymer Concretes against Sulfuric Acid Attack", *Doctoral Thesis,* **School of Civil and Environmental Engineering, University of New South Wales, Sydney, Australia, January 2007**

This doctoral thesis was developed to investigate the characteristics of synthesized fly ash-based geopolymer concretes subjected to a controlled sulfuric acid environment over an 18 month time period. Various testing regimes were performed using the Taguchi experimental design method to determine ultimate mechanical strengths, the degradation process, penetration rates of the acid into the geopolymer matrix and the chemical composition of the formed aluminosilicate structures. Immersion concentrations specified for all test specimens were 10 percent sulfuric acid (H_2SO_4) for 56 days and 1 percent sulfuric acid for a one and a half year period. The acid bath was changed out monthly to maintain concentration levels and the acid volume to specimen surface area ratio was eight.

Two types of geopolymer concretes made from both Eraring fly ash and a mix of Eraring and Kaolite fly ash were created and used for testing analysis. Portland cement concrete was also utilized and evaluated as a control group for comparison. Physical examinations were performed at defined intervals to evaluate their respective sulfate resistances. Additional examinations for corrosion potential were conducted. Pore volume change, acid penetration into the matrix and changes to the aluminosilicate microstructure of the geopolymer gel and were all topics of investigation.

Structural analysis of crystalline phases was performed using x-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS) devices. The analysis of the aluminosilicate structures within the final geopolymer product was conducted with a Magic Angle Spinning-Nuclear Magnetic Resonance (MAS-NMR) machine. Likewise, a Fourier Transform Infrared (FTIR) tool was utilized for Si-O-Al bonding analysis.

Basic visual examinations were conducted at given intervals to address specimen appearance, mass change, compressive strength variations and porosity differences. Furthermore, additional tests were performed to understand the acid diffusion rate into the geopolymer matrix. This test was performed by covering all but one side of the 50 mm^2 cube specimen with epoxy to allow one dimensional penetration over time. Diffusion depths were assessed at time periods of 7, 28, 56, 84, 140, and 180 days. In addition, the mechanisms of degradation were studied, including dry shrinkage, gypsum and ettringite formation due to the presence of calcium in either the fly ash or aggregate mix, ASR swelling, and surface efflorescence deposited by loose alkalis.

Mechanical strength testing was conducted using a Denison machine with a 300 tonne capacity at 150 kN/min crush rate. Flexural testing was performed on 25 x 25 x 285 mm

samples at 28 days of age per ASTM C580. However, the compressive testing was in accordance with the British Standard BS 1881 to accommodate the 50 mm^2 sample size. The compressive sample size was chosen to reduce the required immersion time for adequate acid penetration.

Initial observation of the Eraring samples after 28 day immersion revealed obvious surface efflorescence and a compressive strength of 48 MPa. It was noted that a reduction in alkaline activator could help prevent efflorescence, but it was not suggested due to possible strength reduction of the material. Instead, a partial replacement of the EFA with kaolite ash was attempted. Doing so resulted in greater mechanical strength and a reduction in the required amount of alkaline activator solution. It was stated that the geopolymer materials cured at 70 °C achieved compressive strength of 70 MPa at 28 days, while the specimens cured at ambient temperature achieved only 36 MPa and 58 MPa at seven and 28 days, respectively.

Furthermore, comparisons to Portland cement concrete samples after a period of 18 months yielded significant differences between the two materials. The Portland cement concrete had suffered major dissolution with revealed aggregates after only a 28 day immersion in 1 percent acid (H_2SO_4). The geopolymer material remained intact without any sign of visual degradation or matrix softening. Actual mass loss observations were stated at 5 percent for the geopolymer and 40 percent for the Portland cement concrete. Post-immersion compressive testing was performed on the geopolymer samples, but excessive spalling on the Portland cement cubes prevented a control test from being performed. Residual compressive strengths of the geopolymer were measured at 61-67 percent of their original values after 56 days in 10 percent acid solution; the specimens immersed for 18 months in 1 percent solution yielded 72-90 percent strength measurements. The acid penetration rate into the geopolymer matrix was found to follow Fick's first law of diffusion with a recorded proportionality constant of 1.14 (10 percent H_2SO_4) and 0.556 (1% H_2SO_4).

Additional tests on the affects of adding potassium hydroxide (KOH) as the alkali-activator revealed a strength decrease over concretes created using sodium hydroxide (NaOH). When the KOH concentrations were reduced and sodium hydroxide and sodium silicates were added to compensate, serious cracking was observed while immersed in the sulfuric acid environment, as potassium alum ($KAl(SO_4)$) formation was identified. A comparison with a geopolymer material containing only a sodium hydroxide activator showed no similar cracking of degradation properties. It was therefore recommended that the use of potassium hydroxide as an alkali activator in geopolymer cements be avoided.

Finally, the conclusion was developed that geopolymer concretes consisting of class F fly ash and sodium hydroxide activators are superior to Portland cement concrete as related to sulfuric acid resistance.

BINDER REACTION DEGREE (α)

Palomo, A., and Fernandez-Jimenez, A., "Alkaline Activation of Fly Ashes. Manufacture of Concretes Not Containing Portland Cement", *Institute Eduardo Torroja (CSIC)*. **28033. Madrid. Spain**
> This paper analyzes the mechanisms by which fly ash receives its alkaline activation and relates its use to the precast concrete industry as a viable substitute to Portland cement in concrete applications. Testing of the cured geopolymer specimens include flexural strength

of prisms (15 x 10 x 70 cm), compressive strength on cubic samples (15 cm^2), steel pull-out for adherence, shrinkage to drying, and static loading of railroad mono-block sleeper ties. The geopolymer fly ash resin was prepared with an alkaline dissolution containing 32 percent Na$_2$O, 5 percent SiO$_2$ and 63 percent H$_2$O. It was added to an aggregate mixture comprised of 6-12 mm siliceous aggregate and 0-5-mm washing sand with a fineness modulus of 1.26, an aggregate+sand/fly ash ration of 4:1, and a solution to fly ash ratio of 0.5. All concretes for testing consist of a Spanish (type F) fly ash content of 465 kg/m^3. The aggregate dosages for the railroad sleeper test were 825 kg/m^3 of fine aggregate silica sand, 1050 kg/m^3 of coarse siliceous aggregate. The material produced using activated fly ash via the alkaline process yielded 35.4 MPa (12 hrs) and 50 MPa (20 hrs). The curing temperature directly affects compression strength results. The steel adherence testing in 50 MPa concrete produced breaking values capable of breaking the set steel insert prior to pull-out. Shrinkage of the set mortars was rarely recorded, which is highly beneficial to load capacity and breakage strength. The research validates the use of geopolymer fly ash-based concrete in railroad applications.

Fernandez-Jimenez, A. and Palomo, A., "Characterization of Fly Ashes. Potential Reactivity as Alkaline Cements", *Fuel 82***, pp. 2259-2265, 2003**.
This research was conducted to determine the alkali-activation potential for different Class F fly ash materials and identify the main factors involved in successful reactivity and final strength characteristics. Material investigation was conducted using laser granulometry and Blaine Fineness testing for particle size distribution determination and XRD/^{29}Al MAS-NMR spectrometry for micro and mineralogical analysis. The binder produced consisted of a sand aggregate/fly ash mixture at a 2:1 ratio, activated with an 8 M NaOH solution and was cured in regulated temperatures of 85 °C for a period of 20 hours. Immediately following, the specimens were stored at ambient temperatures of 23 °C with relative humidity of 95 percent for up to 180 days. Compressive strength testing of cured mortar prisms (4 x 4 x 16 cm) was employed at 1, 28 and 180 days to evaluate final reactivity of each activated binder. Finally, pore size distribution measurements were obtained using mercury porosimetry.

It was revealed that the key factors for fly ash reaction potential are the relative silica and vitreous phase contents present in the initial ash material, as well as particle size distribution. It was the the particle size distribution of the ash material that was found to greatly influence reactivity and subsequent strength characteristics. Likewise, the most important chemically related factor of reactivity was the relative silica content. High silica content in the ashes tested yielded greater amounts of aluminosilicate gel and increased mechanical strength. Removal of all ash particles greater than 45 μm increased the one (1) day compressive strength to over 70 MPa. While great strength values were obtained in these samples, even the least recorded compressive value was observed above 30 MPa. For this reason, all ashes tested were found to be suitable for alkali-activation in geopolymer cement products.

Fernandez-Jimenez, A., de la Torre, A.G., Palomo, A., Lopez-Olmo, G., Alonso, M.M., Aranda, M.A.G., "Quantitative Determination of Phases in the Alkali Activation of Fly Ash. Part I. Potential Ash Reactivity", *Fuel 85***, pp. 625-634, 2006.**
This paper focuses upon investigation of two different types of fly ashes for the purpose of identifying the finite vitreous and crystalline entities of each. X-ray diffraction utilizing the Rietveld method, chemical analysis, and nuclear magnetic resonance were all employed for micro evaluation of the ash materials. It was the objective of this research to better

understand the glassy phase compositions and thermal backgrounds of these fly ash samples (labeled sample 'L' and sample 'M') for the purpose of improving current techniques used to select and control alkali/fly ash reactivity within a desired cement mix design. Knowing the intricate properties of a selected fly ash material (and how to extrapolate that data efficiently) is believed to allow for a cement product of improved mechanics and a reduction in trial and error time consumption during design.

Prior to evaluation, each ash specimen was treated with a 1% HF acid solution to dissolve the vitreous phase of the ash, while keeping the crystalline structures intact. Both pre- and post-treatment ash analysis was performed using XRPD and ^{27}Al and ^{29}Si MAS-NMR technologies for comparison. The resulting diffractograms conclude that the samples differed slightly in glassy phase, mullite and quartz composition and that these differences affect the reactive nature of each specimen. The ^{27}Al MAS-NMR spectra revealed a higher tetrahedral-to-octahedral aluminum (A_T/A_O) ratio in ash 'L' than 'M', while 'M' possessed greater mullite content.

These findings confirm the effectiveness of this employed technology to evaluate and categorize the thermal history and SiO_2/Al_2O_3 ratio of a selected fly ash material for use in specific mix designs. It was then concluded that the reactive nature of a fly ash material in an alkali-based solution is directly related to the content of its vitreous and crystalline phases. As well, it was noted that the percentage of aluminum oxide in the fly ash material is essential to a proper and chemically efficient cement design; this research offers an effective method of measuring its presence.

Fernandez-Jimenez, A., de la Torre, A. G., Palomo, A., Lopez-Olmo, G., Alonso, M.M., Aranda, M.A.G., "Quantitative Determination of Phase in the Alkaline Activation of Fly Ash. Part II: Degree of Reaction", *Fuel 85*, **pp. 1960-1969, 2007.**

This paper investigates the reactivity degree of NaOH-activated fly ash materials   using HCl acid for product dissolution and XRPD/NMR analysis for remaining crystalline, vitreous and amorphous phase quantification.

Two different type F fly ash samples (sample L and sample M) were activated with an 8 M NaOH solution in ratios of 0.40 and 0.56, respectively. The resulting paste was stored at 85 °C for seven days in air-tight, plastic bags before being introduced to a 1:20 HCl solution for reaction product dissolution. The remaining residue was then dried at 100 °C prior to being calcined at 1000 °C and the degree of reactivity (α) was quantified and recorded as the overall weight loss of the residue specimen. Testing was performed three times to ensure data corroboration.

It was noted that while initial fly ash samples L and M maintain chemical characteristics similar to one another, they differ greatly in mineral content. Sample L was reported to possess 12 percent mullite and seven percent quartz and sample M consists of 22 percent mullite and 11 percent quartz. It is believed that the mineralogical differences between the two impacted available vitreous alumina and thus, reactive intensities of each ash. The maximum recorded reactivity of sample L was on the order of 64.5 percent, while ash particles in sample M reacted at less than 40 percent; an approximate 25 percent difference. Furthermore, recorded spectra from ^{29}Si MAS-NMR illustrated signals indicative of heterogeneous distribution among the Si atoms. Peaks appeared between -104 and -88 ppm, identifying the presence of unreacted quartz in the form $Q^4(nAl)$: n=0-4.

Product formation from reacted ash particles occur throughout stages deemed dissolution and precipitation, each of which contributes to the creation of Si-O-Al and Si-O-Si bonding. It is stated that while the Si-O-Si bonds are more thermodynamically stable, Si-O-Al bonds are preferred over the latter. For this reason, the Si/Al content of the initial material becomes an important factor in mix design. This confirms the previous statement regarding measured sample reactivity; sample L contained 20.5 percent Al_2O_3 and sample M contained only 14.1 percent Al_2O_3.

It is concluded that the three methods of evaluation employed during this research provide consistent results with a correlating error of less than 5 percent. The methods most accurate were stated to be the XRPD and the acid attack, yet all three were required to produce quantitative results of relevant significance.

Krizan, Darko, Zivanovic, Branislav, "Effects of Dosage and Modulus of Water Glass on Early Hydration of Alkali-Slag Cements", *Cement and Concrete Research 32,* **pp. 1181-1188, 2002.**

The focus of this research was to evaluate early hydration effects of water glass and sodium metasilicate-activated, slag-based cements at room temperature cure. Ratios of water-to-slag and 'n' modulus of the activator present were varied and the results analyzed. Observations for dry shrinkage and mechanical testing for compressive strength at specific curing intervals were conducted and recorded for comparison to the Portland cement control group data.

The granulated blast furnace slag was activated using the following solution: water glass ($Na_2O(n)SiO_2$) and sodium metasilicate (Na_2SiO_3) with an 'n' modulus ratio of 3.01 ($SiO_2:Na_2O$). The aggregate used for mortar composition was quartz sand of (0-2 mm) diameter. The slag mortar produced had a water/binder ratio of 0.43 and the Portland control mortar water/cement ratio was held at (0.5). The mortar was formed into 40 x 40 x 160 mm prisms for compressive testing and allowed to cure at 20 °C (68 °F) in 90 percent relative humidity until testing. Dry shrinkage measurements of the alkali-activated specimens cured at 20 °C in 55 percent RH were taken at four, seven, 14, 28 and 90 days; the PCC specimens were cured in water and observed according to the alkali-slag schedule.

It was concluded, using isothermal conduction calorimeter technology, that the activated cement material experiences two separate heat evolution cycles during its pre-induction period and the magnitude (and duration) of this peak is increased directly by an increase in the activator modulus. Furthermore, the ultimate strength of the alkali-based specimens (0.6-1.5 moduli) was greater than the control group Portland cement. However, the dry shrinkage of the alkali-slag material far exceeded that of PCC and would therefore required additional research prior to regular industry implementation.

Park, Sang-Soon, Kang, Hwa-Young, "Strength and Microscopic Characteristics of Alkali-Activated Fly Ash Cement", *Korean Journal of Chemical Engineering 23, No. 3***, pp. 367-373, 2006.**

This paper investigates activator concentration, curing time and liquid/fly ash ratios as factors pertaining to compressive strength gain within alkali-activated cements and reports characteristics observed from a microscopic perspective. No Portland cement mixes were used in experimentation and analysis of porosity, internal structure and reaction degree were performed utilizing SEM, XRD and MIP technologies.

A class F, low-calcium fly ash was procured from Korea and mixed with sodium hydroxide in a 40-70 percent solid/liquid alkaline ratio and varying alkali concentrations from 1-8 M to create the fresh paste material. The formed binder was poured into 5 cm^3 molds and samples were placed into an oven environment ranging from 20-80 °C for a period of one day until solidified. Specimens were then demolded and allowed to finish activation cure for up to 28 days, depending upon planned regimen.

It was found that the cements produced using a 5-6 M alkaline concentration with alkali/ash ratio of 0.4 and curing temperature of 50 °C was optimum for compressive strength development. Specimens containing low concentrations of sodium hydroxide and/or samples absent from elevated temperature curing were found to maintain low strength values after 28 days and micro analysis showed little crystalline formation at room temperature. An amorphous aluminosilicate gel was observed as the fly ash reaction product, binding the ash particles together in a more dense, less porous matrix. This occurrence was concluded to be the supporting evidence to increased compressive strengths in alkali-activated fly ash cements.

Chen, W., Brouwers, H.J.H., "The Hydration of Slag, Part 1: Reaction Models for Alkali-Activated Slag", *J Mater Sci 42***, pp. 428-443, 2007.**

The purpose of this research was to develop mathematical models capable of quantifying hydration products formed within alkali-activated slag (AAS) mortars and determining their hydrated calcium silicate (C-S-H) composition and chemical shrinkage properties. Retained water of hydration and an overall hydration equation were also derived. It was stated that the main reaction product of hardened AAS paste is C-S-H, followed by hydrotalcite, hydrogarnet, tetracalcium aluminate hydrate, ettringite and AFm phases (C_4AH_{13} and C_2ASH_8). All three proposed models are based upon molar oxide balance between the initial slag material and the final hydration product.

The hydrotalcite, hydrogarnet and ettringite are formed through the combination of the aluminum present in the slag and MgO, Fe_2O_3, and SO_3. Any remaining aluminum is substituted into C-S-H for a lack of available silicon (Si) and ultimately forms the AFm phases. It is noted that this formation is more likely to occur from slags high in Al_2O_3 and low in MgO. While C-S-H accounts for the product majority, it is believed that the presence of the aforementioned substances has an effect on final composition.

The models created are stated to calculate retained water within the hydration products, quantify those products and determine the overall composition of the C-S-H within the matrix. It was noted that the models have been tested against experimental data and are aligned with their results.

It was found that chemical shrinkage due to hydration was much greater in ASS than in ordinary PCC products and that the shrinkage observed is a direct correlation to the hydration degree. This shrinkage increases pore volume in the paste and is believed to inflict internal stress in the cement mixture. Porosity, pore distribution, and pore connectivity can negatively affect its mechanical performance. It is concluded that while ASS requires a larger water to binder ratio for full hydration, the secondary effects of chemical shrinkage, as a direct result, must be closely monitored.

Hilbig, H., Buchwald, A., "The Effect of Activator Concentration on Reaction Degree and Structure Formation of Alkali-Activated Ground Granulated Blast Furnace Slag", *J Mater Sci 41***, pp. 6488-6491, 2006.**

This paper discusses the resulting reaction degree and structural behavior of activated, blast furnace slag pastes relative to variable alkaline concentrations. The slag used for analysis contained 73 percent (by weight) amorphous phase glass and phases of crystalline calcium silicates and calcite. Additionally, it was reported that Portland cement and limestone were also present.

Sodium hydroxide was used for slag activation in concentration ranging from 3.4 percent to 13.6 percent (by weight of slag) with a water/slag ratio of 0.33. Prismatic molds of 1 x 1 x 6 cm were constructed and left to cure for 24 hours at 40 °C prior being stored over a water bath at ambient temperatures until testing commenced.

The initial slag material and the formed pastes were both analyzed using nuclear magnetic resonance spectroscopy (^{29}Si and ^{27}Al NMR) and x-ray diffractometry (XRD). It was noted that the ^{27}Al MAS-NMR evaluation is the most suitable for detecting and quantifying silicate phases.

It was found that elevated NaOH concentrations resulted in greater reaction degrees within the pastes. Alkali activation was determined not to be a catalyst mechanism, but instead fully dependent upon the amount of water available and the content level of soluble glass in the slag mix.

Song, S., Sohn, D., Jennings, H.M., Mason, T.O., "Hydration of Alkali-Activated Ground Granulated Blast Furnace Slag", *Journal of Materials Science 35***, pp. 249-257, 2000.**

This research investigates the use of ground granulated blast furnace slag (GGBFS) as a pozzolanic material in alkaline activated cement binders. Experimentation consisted of binder creation under a controlled pH environment and cure at 25 °C for a maximum of 28 days, followed by detailed analysis of porosity as related to initial pH levels using impedance spectroscopy (IS), heat evolution during alkaline reaction via isothermal calorimetry and microstructure evaluation of the resulting matrices by environmental secondary electron microscopy (ESEM).

The slag product obtained for testing had a Blaine Fineness of 5565 cm^2/g and was mixed with deionized water and (1 M and 0.1 M) NaOH solutions at a mass ratio of 0.45 (solution/slag). Resulting binders were tube molded and sealed prior to being immersed in a 25 °C water bath. Fresh pastes were subject to calorimetry measurements to obtain heat evolution rates and IS was used for electrical conductance observation. Once rigid, cut samples were taken intermittently from the molds for solvent exchange experimentation using a methanol bath for pore volume determination.

It was empirically calculated that the concentration of the alkaline solution is inversely proportional to the solvent-accessible porosity (given as φ_{MeOH}); higher concentrations of alkali produced matrices of lower porosity. Additionally, the GGBFS pastes tested were found to be more porous than equivalent PCC pastes. The required pH level of the initial binder system was found to be 11.5 for effective GGBFS reaction and hydration. Finally, it was concluded that the initial pH balance of the binder system (NaOH concentration) plays a crucial role in determining final geopolymer properties.

Fernandez-Jimenez, A., Puertas, F., "Alkali-Activated Slag Cements: Kinetic Studies", *Cement and Concrete Research 27*, **No. 3, pp. 359-368, 1997.**

This study investigates the reaction degree and hydration kinetics within ASS binders by means of conduction calorimetry and the Stutter method. Blast furnace slag was activated using a mixture of commercial water glass and a 4.62 N NaOH solution with an alkali modulus of 1.5 and a pH of 13.22. The mechanism of reaction within the paste was determined and an activation energy value was obtained. The activating solution/slag mixture was maintained at a constant 0.4 weight ratio. Calorimetry testing occurred at a set time interval of 45 hours and at the following hydration temperatures: 25, 35, 45 and 60 °C.

In the early stages of hydration (25 °C), five discernible steps were identified through the empirical curve: slag partial dissolution, induction, acceleration, deceleration and decay. The first step was observed within the first five minutes of hydration and is represented by the first curve peak. The induction period was noticed to maintain a low reaction rate and the acceleration and deceleration periods were associated with mass precipitation of a hydrated calcium silicate gel. These periods represent the second curve peak. The final step of hydration observed was another period of low reactivity and hydration finish. It was also noted that temperature directly affects the duration and intensity of these steps.

It was concluded that slag activation occurs rapidly with the second curve peak being witnesses within the first ten (10) hours. Due to this accelerated paste evolution, completed reactions within the paste are seldom observed and a constant heat of hydration is difficult to obtain. However, it was confirmed that all hydration reactions beyond the induction phase occur via a diffusion mechanism regarding a product layer surrounding the remaining anhydrous slag particles. It was stated that the equation best representing the current work was that of W. Jander, as referenced in the publication. The activation energy for the diffusion process was determined to be 57.6 KJ/mol.

FIBER REINFORCEMENT

Silva, F.J., and Thaumaturgo, C., "Fiber Reinforcement and Fracture Response in Geopolymer Mortars", *Fatigue Fract Engng Mater Struct 26*, **pp. 167-172, 2002.**

This paper describes using wollastonite fibers as a reinforcement element in poly(sialate-siloxo) (PSS) geopolymer to improve the toughness factor of the mortar mix. The toughness properties were determined using of Non-Linear Fracture Mechanics (NLFM) techniques. The mortar composites tested had a Si/Al ratio of three and were reinforced with wollstonite micro-fibers of volumes from V_f=0 percent to V_f=5percent. The K_I curves (stress intensity factor) and K_{IC} fracture parameters were calculated and compared to Portland cement composites. It was found that a fiber volume of 2 percent yielded the best K_{IC} and Δa_c (effective crack extension) and improved the fracture toughness. It is concluded that the PSS cement can substitute for traditional Portland cements in structural applications.

Tiesong Lin, Dechang Jia, Peigang He, Meirong Wang, Defu Liang, "Effects of Fiber Length on Mechanical Properties and Fracture Behavior on Short Carbon Fiber Reinforced Geopolymer Matrix Composites", *Materials Science and Engineering A* **(2008), D01:10.1016/j.msea.2008.06.040**

This research explores improvement of geopolymer mechanical properties though implementation of short carbon fiber reinforcement in the material mix. The base resin was created by dissolving silica solution into a KOH solution. Metakaoline was formed by

heating kaolin powder to 800 °C for 2 hours. It was added to the potassium silicate solution and mixed for 30 minutes using a high-shear mixer. The short carbon fibers of nominal lengths (2, 7 and 12-mm) were separated using ultrasound in ethanol and filtered out using a wire sieve to create sheet-like fiber performs. This method of separation provides a uniform distribution of carbon fibers in the mix. The preforms were impregnated with the resin and stacked thirty layers deep to create the test mold. The molds were placed into a vacuum bag at 80 °C for 48 hours to eliminate air voids between layers and then cured at 120 °C for 24 hours. The cured molds were tested for flexural strength using a three-point bending fixture. Six specimens were tested under each condition and observed by optical microscope for surface micrographs and a scanning electron microscopy was used for fracture surfaces. Bend testing resulted in deformation of the specimens but no breaking occurred, which suggests non-catastrophic fracture behavior. The C_f/geopolymer composites exhibited non-linear elastic increase of load until maximum load was reached, typical of pseudoplasticity behavior. The 7 mm fiber length sample produced maximum flexural strength and work of fracture values, increased by 4.4 times and 118 times, respectively over the fiber-free geopolymer matrix. It was concluded that strengthening and toughness mechanisms of the carbon fiber reinforced samples was attributed to the fiber bridging and pulling-out resistance within the geopolymer resin.

ALKALI-SILICA REACTIONS (ASR)

Garcia-Loderio, I., Palomo, A., Fernandez-Jimenez, A., "Alkali-Aggregate Reaction in Activated Fly Ash Systems", *Cement and Concrete Research 37*, **pp. 175-183, 2007.**
  This paper discusses the internal expansion potential of cementitious systems based on activated fly ash as related to alkali-silica reactions (ASR) and compare its behavior to that of ordinary Portland cement concrete. The methods used to evaluate the ASR in each specimen are based upon ASTM C1260-94 which estimates deterioration in the cement mortars within a 16 day period. Three series of prismatic mortar specimens (PCC and FA) were produced: 100 percent siliceous aggregate, 100 percent opal aggregate, 90:10 (by weight) siliceous+opal aggregate mix; a control specimen of Portland cement mortar and a Portland cement-free mortar were also produced.

  The PCC mortars were cured at 21 °C with 99 percent humidity for 24 hours prior to an immersion bath at 85 °C for additional 24 hours. The alkali-activated fly ash specimens were produced using 8 M NaOH solution and cured at 85 °C for 20 hours in high humidity conditions. Routine measurements were taken during the curing process to verify potential expansion properties. At 16 and 90 days, detailed analysis was performed on the cured materials via energy dispersive microanalysis and diffractometer data.

  The series using 100 percent siliceous aggregate resulted in significant expansion of the PCC1 and subsequent specimen cracking between the the 16 and 90 day interval. The FA specimen experienced no visual deterioration and was found to have only generated the reaction product typical of the alkaline activation process. The 16-day PCC mortar was found to have a presence of a high-sodium gel at the aggregate interface and a 90-day analysis of the same sample revealed many ASR-induced microcracks.

  For the 100 percent opal aggregate samples, an x-ray diffractometer was used to analyze the PCC2 specimen at the 16-day period. It was noted per the diffraction graph that the disappearance of the silica products (opal, quartz) in the aggregate suggests that they were

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attacked and dissolved. Furthermore, the quantity of portlandite in PCC2 was found to be far greater at 16-days than in the PCC1 mix. An ASR product was clearly evident with a rosette-type morphology.

The silica-opal aggregate mix analysis revealed similar results to the PCC1 mix; the graphs of both indicate a sharp decline in portlandite peaks throughout the testing indicating calcium uptake by the gel produced during the alkali-silica reaction. It was also noticed that the plagioclase signal intensity declined, illustrating an aggregate attack. The FA3 specimen diffractograms (much like FA1 graphs) showed mainly the presence of zeolitic compounds at 16-days, but much larger amounts than FA1 at the 90-day analysis. Zeolites maintain the ability to permeate into the pre-existing void matrix within the specimen, thus avioding internal stresses that could possible lead to microcracking. Therefore, no visual damage of the FA3 specimen was observed at either of the two analysis periods. Conversely, the PCC3 sample greatly exceeded the expansion limit at 90-days and was severely deformed from cracking due to the large amounts of ASR products (rod and rosette-type morphologies) within the matrix.

It was concluded that the FA-based, alkali-activated mortars are less susceptible to alkali-silica reactions than the standard Portland cement based concretes. This research indicates that the presence of calcium directly affects the expansive nature of the formed gels.

Fernandez-Jimenez, A., Puertas, F., "The Alkali-Silica Reaction in Alkali-Activated Granulated Slag Mortars with Reactive Aggregate", *Cement and Concrete Research 32*, **pp. 1019-1024, 2002.**

This paper focused upon the expansion potential of alkali-activate blast furnace slag (AAS) cement mortars mixed with reactive siliceous aggregates and compared the results to control group data of standard Portland cement mortars under the same conditions. The activator used was a NaOH solution with 4 percent Na_2O (by slag mass) and the method of testing was per ASTM C1260-94 and NBRI Accelerated Test Method. The resulting ASR products were evaluated using SEM/EDX technology. While the standard specifies a 16-day test period, this analysis was conducted for 140 consecutive days.

A slag/opaline aggregate ratio of 1:2.25 was used for the mortar samples. The (2.5 x 2.5 x 23 cm) molded specimens were cured under 99 percent humidity at 25 °C for 24 hours. Once fully cured, an initial measurement was taken of the samples prior to entry into one of two immersion liquids at 80 °C: deionized water (reference liquid) and 1 N NaOH. The immersed specimens were periodically measured for expansion/contraction over the 140 day test duration. As well, SEM/EDX analysis was conducted at the end of the test regime.

Two main factors were observed during testing: specimen expansion and/or contraction and the change in specimen mass over time. It is noted that the slag mortars in the alkaline solution bath shrank before finally expanding and the slag specimen in deionized water showed little to no overall expansion effects. Coincidentally, the AAS mortar in NaOH decreased in weight prior to a steady weight gain throughout the test period. The initial loss of weight is attributed to possible exudation of tobermorite-type gels from the specimen into the surrounding solution, as an increase in densification of the NaOH solution was simultaneously observed.

Of the specimens immersed in deionized water, the PCC expanded the most at 0.05 percent and the AAS expanded 0.02 percent due to the lack of alkalis available for reaction in the

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water. Furthermore, an SEM/EDX microanalysis showed no ASR products existed in the AAS specimen. The cause for an absent ASR was explained as a competition for Na^+ ions between the slag and the potential ASR. Without the presence of free Ca^{2+} ions (as predominant in Portland cement), an alumina-silicate reaction was minimal and the AAS specimen showed minimal expansion.

In the alkali immersion, it was found that both specimens expanded. The PCC mortar began expanding immediately in the presence of the 1 N NaOH solution to 0.08 percent within the first 16-days. After 20-days, the deleterious limit of 0.10 percent (as stated in ASTM C1260) was exceeded. An SEM/EDX analysis showed formations of massive sodium and calcium silicate gel morphologies within the matrix. The AAS samples expanded less than the PCC due to the competition between the slag and aggregate entities for the alkalis and available Ca^{2+} ions. The recorded crystallization in the AAS specimens was of bar- and rosette-type morphology.

It is noted too, that the Accelerated Test Method is insufficient for testing for ASR-induced expansion in AAS mortars due to the limiting factor of a 16-day test regime. Achieving deleterious data for an AAS specimen with this time period is doubtful and may therefore yield misleading results. It is recommended that a test period for longer than six months be conducted to successfully determine the expansion effects of ASR within alkali-activated cement mortars.

GEOPOLYMER DURABILITY

Fernandez-Jimenez, A., Garcia-Lodeiro, I., Palomo, A., "Durability of Alkali-Activated Fly Ash Cementitious Materials", *J Mater Sci*, 42-3055-3065, 2007.
This paper addresses the durability of alkali-activated fly ash cement material with respect to several aggressive environments: controlled seawater, sodium sulfate, hydrochloric acid, and deionized water (as a control). Observations regarding alkali-silicate induced expansion (per ASTM C1260-94) and weight loss were monitored and testing regimes including compressive strength and microstructural analysis were conducted. All specimens were created using a Spanish-style, class F (per ASTM C618-03) fly ash. Control mortars were constructed of Type I Portland cement. Two different activating solutions were employed: 'N' (8 M NaOH) and 'W' (85 percent 12.5 M NaOH, 15 percent sodium silicate with SiO_2/Na_2O ratio of 0.16.

Testing for chemical resistance was performed on (4 x 4 x 16 cm^3) prisms. The specimens were cured for 20 hours in 99 percent humidity at 85 °C prior to being immersed in their respective environments. Testing was performed at seven, 28, 56, 90, 180, 270 and 365 days from time of immersion. Intermediate tests performed were compressive and bending strength and each specimen received mineralogical characterization before re-entering the environmental bath.

The acidic environment was created using a 0.1 N HCl solution with a 1.0 pH level, which was periodically replaced to ensure a continuous normality throughout the testing period. The specimens were three cm^3 by volume and a control specimen constructed of Portland cement was used. Mechanical testing, mineralogical characterizations and weight variation analysis were performed at seven, 28, 56 and 90 days.

Additional specimens of (2.5 x 2.5 x 28.5 cm^3) were created for testing alkali-silica reactions. The aggregate used was a siliceous mineral considered in Spain to be non-reactive. Molds were cured for 20 hours in 99 percent humidity at 85 °C prior to being immersed in a 1 M NaOH solution for 16 days. Periodic measurements of length were recorded to analyze the effects of potential alumina-silicate reaction (ASR) induced expansion. As well, EDX and SEM/EDX testing was performed to identify microstructural characteristics.

It was found that the 'W' mix in sulfates and seawater was more mechanically sound that the 'N' mix. This was attributed to to formation of gel and zeolite crystals from high levels of silicate ions present in the immersion causing a more compact, gel-rich structure to form.

The acidity tests revealed a degradation of the Portland control specimens (9.8 percent mass loss), while the AAFA 'W' and 'N' samples only experienced a loss of 4.2 percent and 2.5 percent, respectively. The degradation observed was reported to be due to an aluminosilicate depolymerization followed by silicon-enriched polymeric ion condensation within the matricies. The PCC matrix lost a total of 47 percent of its original compressive strength, while the AAFA specimens only saw a 25 percent maximum loss.

Finally, the AAFA materials passed the 16 day expansion threshold requirement of less than 0.10 percent expansion (per ASTM 1260-94), however, a continued testing period revealed additional expansion at 180 days which exceeded the mandated ceiling. It was noted though that the AAFA specimens were superior to the PCC materials with respect to sodium-calcium silicate gel expansion characteristics. It was also recorded that SEM observations showed zeolite crystal precipitation into voided pores had occurred, likely benefiting the mechanical properties of the matrix.

AMBIENT/ELEVATED TEMPERATURE CURING

Fernandez-Jimenez, Ana, Palomo, Angel, Pastor, Jose Y., Martin, Antonia, "New Cementitious Materials Based on Alkali-Activated Fly Ash: Performance at High Temperatures", *Journal of the American Ceramic Society XX*, **pp. 1-7, 2008.**

This research focuses upon the comparative mechanical performance characteristics between commercial Portland cement and activated fly ash materials subjected to extreme curing temperatures. Post-exposure mineralogical and microstructural analysis was performed using differential thermogravimetry (DTG), fourier transform infrared (FTIR), and x-ray diffraction technologies. Testing was conducted from the perspective of specimen compressive and bending strength and toughness both during and after temperature extremes. Temperatures ranging from 25 °C to 600 °C were maintained for the heated tests, while post-exposure test samples experienced temperatures to 1000 °C for one hour prior to receiving compressive analysis.

The Portland cement paste was mixed at water/cement ratio of 0.27 (by mass) and the fly ash material was activated using an 8 M NaOH solution with alkaline/ash ratio of 0.25 (by mass). For each paste series, three different mold types were prepared for two separate test regimes: 8 x 4 x 50 mm / 5 x 5 x 10 mm prismatic specimens for high-temperature mechanical testing and 10 x 10 x 60 mm prisms for post-thermal treatment analysis. All Portland cement samples were cured for 20 hours at ambient temperatures (22±1 °C) and a 98 percent relative humidity (RH) prior to being demolded and stored within the curing chamber for an

additional 28 days. The fly ash specimens were cured at 50 °C for four hours with a 90 percent RH and then further cured at 85 °C for 16 hours at the same RH level.

Testing results revealed a thermal advantage for alkali-activated fly ash cements over comparable Portland cement materials. The recorded bending strength of the activated system remained the same under the extreme heat environment, while the material created from Portland cement saw a 33 percent decline in bending strength at 400 °C. Likewise, the compressive strength of the fly ash specimens increased rapidly with temperature increase and the Portland samples developed a residual compressive strength past 800 °C. The toughness measured for each was similar at ambient temperatures, however, the Portland mix fell to 50 percent of initial toughness values at 600 °C; the fly ash material remained unchanged to this temperature. Thermo-gravimetric analysis found a much greater water weight loss in the Portland series than in the fly ash models at 450 °C and a post-exposure visual inspection of each showed macro cracking and separated material fragments from the Portland samples. The fly ash cements were found to retain their mechanical and thermal resistance properties at temperature far better than the Portland cements under extreme heat conditions.

Zuda, Lucie, Rovnanik, Pavel, Bayer, Patrik, Cerny, Robert, "Effect of High Temperatures on the Properties of Activated Aluminosilicate with Electrical Porcelain Filler", *International Journal of Thermophysics 29***, pp. 693-705, 2008.**

A research experiment to analyze the mechanical and thermal properties of alkali-activated aluminosilicate materials containing electrical porcelain filler and exposed to high temperatures was conducted. Testing regimes included thermal loading of slag-based specimens to 1200 °C and final analysis was performed using mercury intrusion porosimetry (MIP) and scanning electron microscopy (SEM). Compressive and bending strength, thermal conductivity and specific heat capacity was measured for each tested specimen and compared to reference data.

Fine ground blast furnace slag was obtained from the Czech Republic and activated with a water glass solution. The electrical filler material was used in place of fine aggregates. The resulting paste mix was vibrated into molds and left to sit for 24 hours prior to being water bath cured for 27 additional days at ambient lab temperatures. Specimens were then dried at 110 °C before being exposed to their applicable testing temperatures of 200, 400, 600, 800, 1000 and 1200 °C with a heat gain rate of 10 K/min.

Test results showed a 30 percent decrease in compressive strength and a 20 percent decrease in bending strengths for samples exposed to the 600 °C thermal pre-treatment scenario. However, testing to temperatures of 1200 °C resulted in compressive strengths reaching a factor of two greater than those exempt from heat treatment and bending strengths increased by a factor of six. This was explained as a result of ceramic bond formation combined with akermanite crystallization ($Ca_2MgSi_2O_7$) within the matrix which is known for high thermal resistance. It was concluded that aluminosilicate activated cements containing electrical porcelain filler materials possess characteristics for potential use in high-temperature applications.

Singh, Puyam S., Trigg, Mark, Burgar, Iko, Bastow, Timothy, "Geopolymer Formation Processes at Room Temperature Studied by ^{29}Si and ^{27}Al MAS-NMR", *Material Science and Engineering A 396,* **pp. 392-402, 2005.**

This study of geopolymer cement focuses solely upon formation reactions and material characteristics developed by curing at room temperature. Sodium orthosilicate and two types of sodium silicate solutions were mixed with metakaoline (created by heating raw kaoline to 750 °C for 10 hours) and an alkaline solution to create the geopolymer pastes used for testing. An additional source of silicate anions produced by the reaction between colloidal silica and aqueous alkali was also studied.

MAS-NMR analysis results were obtained by using either a Bruker Avance 400 or Varian Unity Plus 300 spectrometer device. It was found that the reaction of metakaoline with both alkaline activators (NaOH and Na_4SiO_4) yielded incomplete geopolymerization as a result of absent polycondensation reaction indicators. Conversely, the reaction analysis of metakaoline with colloidal silica in the same alkaline environment revealed ^{29}Si and ^{27}Al MAS-NMR spectra typical of geopolymerization products. However, cured specimens of a metakaoline mixed with both sodium silicate and NaOH yielded a material with [29]Si spectra in line with traditional geopolymers, but with a wider ^{27}Al NMR peak. Finally, reactions between metakaoline and the silicate solution (absent of NaOH) slowly formed a hydrolyzed aluminate species, but polycondensation was again incomplete.

Zuda, L., Pavlik Z., Rovnanikova, P., Bayer, P., Cerny, R., "Properties of Alkali Activated Aluminosilicate Material after Thermal Load", *International Journal of Thermophysics 27, No. 4***, pp. 1250-1263, 2006.**

This paper presents experimental data relevant to the resulting properties of an alkali-activated slag system subjected to thermal loading for a defined period of time. Mechanical evaluation of the heated specimens, as well as mineralogical and microstructural analysis was performed and the results compared to reference subjects absent from the loading. Temperatures up to 1200 °C were applied and samples were investigated for resulting porosity, bulk density, compressive strength, bending strength, thermal conductivity and specific heat capacity. Detailed observations were conducted with x-ray diffractometry and scanning electron microscopy.

A fine ground slag material was obtained from the Czech Republic and activated using a water glass solution from dried sodium silicate. The paste was mixed with sand aggregates to create a mortar and placed into 71 mm^3 molds for thermal testing and 40 x 40 x 160 mm molds for mechanical objectives. All specimens were vibrated and stored for 24 hours, demolded and fully cured in a water bath at ambient lab conditions for an additional 27 days. Cured specimens were dried at 110 °C prior to being exposed to the planned thermal loads of 200, 400, 600, 800, 1000, and 1200 °C for a period of two hours. Three specimens were tested for each corresponding temperature interval.

Empirical data revealed an increase in porosity in specimens as the thermal loading increased, with maximum porosity witnessed at temperatures of 600 °C. Minor changes were observed beyond this temperature value. Compressive and bending strengths both achieved a minimum at the 800 °C interval, but began to increase up to the final 1200 °C range. However, strength values were still reported less than the control group absent from loading: 12 percent lower for compression and 18 percent lower for bending. A decrease in thermal conductivity was also found at the 600 °C level with further decreases at the temperature

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increased. At 600 °C, an x-ray analysis revealed the CSH product beginning to transition to a akermanite structure with superior mechanical characteristics to the original pre-thermal load specimens. By 1200 °C, the porosity and mechanical properties had increased greatly and the binder transition was apparently complete. It was then concluded that the tested material maintains potential for use as a fire protection material or in commercial applications requiring heat insulation.

Bakharev, T., "Thermal Behaviour of Geopolymers Prepared Using Class F Fly Ash and Elevated Temperature Curing", *Cement and Concrete Research 36***, pp. 1134-1147, 2006.**

This research paper analyzes the mechanics and thermal properties of alkali-activated class F fly ash materials once subjected to extreme temperatures for definitive periods of time. Cured specimens were heated to temperatures of up to 1200 °C prior to being tested for strength, deterioration and geometric shrinkage. Technologies utilized to evaluate the final product at a microscopic/mineralogical level included x-ray diffraction, thermal gravimetric analysis (TGA), and SEM (BEI)/MIP for porosity validation.

Two separate fly ash materials were obtained for testing: both from Australia industry. FA1 was found be mostly glass with some mullite, hematite and quartz with nominal particles sizes of 1-7 μm in diameter. FA2 boasted similar glass properties, but differed in mullite and quartz content and maintained particles sizes slightly larger at 1-10 μm. Sodium hydroxide (NaOH) and potassium hydroxide (KOH), sodium silicate (type D with M_s) and potassium silicate were all used for different activation regimes. As such, two separate series of test samples were prepared, varying in composition and mold methods. Series 1 consisted of sodium hydroxide, potassium silicate and sodium silicate solutions with water/binder ratios of 0.27-0.345 (by mass). The formed paste was cast into plastic cylinders and sealed. Series 2 specimens were constructed of similar activating agents, but possessed water/binder ratios of 0.09-0.166 and were compacted with pressures from 1-10 MPa, prior to being molded in plastic cylinders and sealed. Curing for both series were identical: 24 hours at room temperature, then temperatures ramped to either 80 °C or 100 °C for a respective specimen and held for another 24 hours. Samples remained in oven for the cooling period and then returned to room temperature until testing.

Cooled specimens were exposed to firing temperatures of 800, 1000, and 1200 °C for a time of four hours. Three specimens were fired for each temperature point and temperature increases were maintained at 10 °C/min for the firing duration. Compressive tests and dimensional analysis were performed both before and after firing for comparative results.

It was found that the thermal stability properties of the samples containing sodium performed less than those of mixed fly ash and potassium. The sodium specimens were observed to rapidly deteriorate at 800 °C, while the potassium mixes remained amorphous to the 1200 °C interval and tested well in compressive analysis. It was found that the sodium mixes developed an increase in overall pore size, thus resulting in a decreased compressive strength value. The compaction samples showed great resistance to shrinkage, but a final conclusion was adopted omitting the tested mix designs from use in commercial industry as related to refractory insulation.

L.Y. Kong, Daniel and Sanjayan, Jay, G., "Damage Behavior of Geopolymer Composites Exposed to Elevated Temperatures", *Cement and Concrete Composites* Vol. 30, Issue 10, pp.986-991, 2008.

The thermal stability of alkali-activated (class F) fly ash-based concretes was studied with regard to strength loss and degradation at extreme temperatures. A total of fifteen (15) separate geopolymer mixes utilizing four aggregate types were tested and formed specimen samples were subjected to controlled heat up to 800 °C for detailed evaluation. The ash materials were activated using grade D sodium silicate of Na_2O/SiO_2 ratio 2.0 and 7 M potassium hydroxide solutions. Two separate aggregates (crushed basalt and blast furnace slag) were added to the activated paste mixtures in a ratio of 60 percent coarse to 40 percent fines. The maximum aggregate size was 14 mm and fine aggregates had a fineness modulus of 1.82. Paste mixtures were formed into 25 mm^3 molds, while the fly ash/aggregate concrete courses were molded as 100 x 200 mm cylinders; both were vibrated and sealed to prevent water loss through evaporation. Both mold types were left for 24 hours in ambient temperatures prior to be moved to curing temperatures of 80 °C for a further 24 hour time interval. At two days, the cure temperature was gradually increased to 800 °C at a rate of 5 °C/min and held for 60 min before being allowed to cool to ambient naturally. A control group specimen series was left at room temperature over the course of curing for direct comparison to the heated samples.

Compressive strength and test evaluation regimes were employed with regard to the following perspective factors: elevated temperature cure, sodium silicate/potassium hydroxide ratios, fly ash/alkaline silicate ratios, geopolymer age, curing intervals, geopolymer/aggregate composite behavior and thermal contraction and/or contraction of the paste and aggregate entities.

Detailed observation of three and seven day specimens revealed a 2 percent volume reduction and no visual cracking. Mass reduction of 13 percent was noted to be lower than metakaolin-based geopolymers which can experience 30 percent mass reduction. Compressive strength analysis showed an increase in overall strength relative to increased Na_2SiO_3/KOH ratios in the paste mix. Conversely, a strength decrease was recorded as a result of lowered fly ash/activator ratios. An explanation for this behavior was given as reaction dilution caused from excess water content within the increased activator volume.

Geopolymer age was found to be of little importance, as geolpolymers attain roughly 70 percent of their compressive strength within the first three to four days of curing. This characteristic was found to directly contradict the behavior of Portland cement concrete, which achieves its strength over time.

Aggregate addition was found to increase the compressive strength of the geopolymer paste prior to heating. Ambient specimens containing basalt aggregates were recorded to improve strength values from 59.0 MPa to 70.5 MPa, while slag aggregate specimens saw a 4.7 percent increase from 59.0 MPa to 61.8 MPa. However, a strength decrease was observed in all samples after being exposed to extreme heat. Post-heat test results show a 58 percent strength loss in the basalt samples and a 65 percent loss in the slag composites, which is far less than the values obtained from the unexposed control group. The contrast in strength behavior was hypothesized to be a thermal expansion correlation between the paste and aggregate bodies. Further testing to include thermogravimetric analysis (TGA) and dilaometry measurements was conducted to analyze this phenomenon. It was found that the

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geopolymer/aggregate composite experienced substantial water loss and subsequent shrinkage at temperatures in the 220 °C to 300 °C range. Separate aggregate testing revealed thermal expansion in all cases at this temperature range. It was finally concluded that thermal incompatibility between the contracting paste and expanding aggregate bodies at elevated temperatures was the direct cause of the strength decrease in test specimens.

POZZOLANIC MIXTURE ANALYSIS (FA/SLAG/METAKAOLIN)

Chareerat, T., Lee-Anansaksiri, A., Chindaprasirt, P., "Synthesis of High Calcium Fly Ash and Calcined Kaoline Geopolymer Mortar", *International Conference on Pozzolan, Concrete and Geopolymer,* **Khhon Kaen, Thailand, May 24-25, 2006.**

This paper researches the intrinsic properties of geopolymer cement mortars as pertaining to cure time and temperature, kaoline production methods and the resulting mechanics from varying pozzolan ratios within the mix design.

The fly ash used was from a power station in northern Thailand, while the kaolin used to create calcined kaolin (CK) came from Ranong in the South. The activating solution was comprised of 10 M NaOH (sodium hydroxide) and sodium silicate as 15.32 percent Na_2O, 32.87 percent SiO_2, and 51.81 percent water (by mass) in a 1:1 ratio. A saturated surface dry (SSD) local river sand used (2.75 sand/binder ratio) to complete the test mortar and specimens were molded as 50 mm^3 cubes.

Multiple test regimes were conducted to determine the optimum variables for kaolin burn temperature and time, mortar curing temperature, CK/fly ash mix ratios, and delay time prior to heat cure. The kaolin samples were divided and subject to testing under high heat in the range of 400-800 °C for up to six hours. It was concluded that the optimum temperature and duration for calcined kaolin production is 600 °C for a period of two hours; additional time at this temperature reduced the final compressive strength of the specimen.

Replacement of a percentage of fly ash with the newly formed calcined kaolin (CK) had effect on the compressive strength of the resulting mortar. Testing revealed that a 25 percent CK replacement yielded a maximum compressive strength of ±43 MPa, while CK values in the 10-40 percent range produced strong material; greater than 40 percent replacement reduced mortar strength.

Additional testing showed that geopolymer samples allowed to rest at ambient temperatures for a period of one to two hours prior to heated cure improved compressive strength measurement values. Testing data from a compressive specimen sent immediately to heated cure showed 34 MPa strength, while samples allowed to remain at room temperature before curing increased to 43 MPa. However, delay times of three to six hours decreased final compressive strength.

Fernandez-Jimenez, A., Monzo, M., Vicent, M., Barba, A., Palomo, A., "Alkaline Activation of Metakaolin-Fly Ash Mixtures: Obtain of Zeoceramics and Zeocements", *Microporous and Mesoporous Materials 108***, pp. 41-49, 2008.**

The intent of this paper was to study resulting characteristics of hardened alkali-activated cements using calcined metakaolin alone (M) and a 1:1 fly ash/calcined metakaolin mixture (FM), both cured at various temperatures for comparison. A sodium hydroxide (NaOH) and sodium silica solution (7.4 percent Na_2O, 1.5 percent SiO_2, 91.1 percent H_2O) was used at a ratio of 1.250 (M) and 0.875 (FM) to activate each respective mixture. The metakaolin used

was formed from kaolin by heating at 750 °C for 20 hours and the fly ash was obtained from a power plant in Lada, Spain.

Prism molds of dimension (10 x 10 x 60 mm) were created and originally subjected to three hours at 85 °C in 98 percent relative humidity (RH). Specimens then underwent five additional curing hours at various temperatures of 85 °C, 150 °C, and 200 °C. Prior to compressive testing at a rate of 2.4 kN/s, the specimens finally rested at ambient for 24 hours in 90 percent RH.

Microscopic structural observation and mineralogical composition was obtained using the following devices: x-ray diffraction, Fourier Transform Infrared Spectroscopy (FTIR), scanning electron microscopy (SEM), and ^{29}Si MAS-NMR technology. Several interesting observations were made of each sample type. It was noticed that the FM material cured at 150 °C for five hours gained the highest strength (29 MPa), while exhibiting the lowest reaction percentage. This was explained as being a product of two separate factors: the presence of the fly ash allowed for an increased gel/zeolite ratio and the unreacted fly ash particles acted as small aggregates, thus enhancing compressive strength properties in the otherwise weaker matrix. Furthermore, there was a tenancy for the formed zeolites to move into and inhabit the hollow shell of the reacted fly ash particles, which decreased available voids and improved mechanics. The MAS-NMR signal analysis also revealed formations crystalline zeolites of high Si/Al ratios within the FM samples which positively affect mechanical strength values. Therefore, despite the lower number of reactive fly ash particles in the FM samples, its Si-rich zeolite formations gave it an advantage over the M product.

It was concluded that time and temperature directly affects the mechanical characteristics of fly ash activated cements. Increased temperatures and longer curing times have shown better performance in all specimens. However, it was also noted that each matrix bears a peak temperature to which the resulting performance is limited. For these trials, the optimum temperature for CCM samples was between 150 °C and 200 °C. Curing temperatures beyond that point have been reported to weaken the material and cause adverse affects to its final compressive strength.

Buchwald, A., Hilbig, H., Kaps, Ch., "Alkali-Activated Metakolin-Slag Blends – Performance and Structure in Dependance of their Composition", *Journal of Materials Science 42*, **pp. 3024-3032, 2007.**

This paper discusses results obtained from geopolymerization using a blast furnace slag and metokaolin mixture as the pozzolanic ingredient. The binder was activated with a sodium hydroxide solution and special attention was paid to determine type and quantity of the reaction products formed by each substance. It was the intent of this research to understand how material products formed by both metakaolin and the slag chemically interact with one another, or if in fact, they evolve separately. ^{29}Si and ^{27}Al MAS-NMR spectroscopy was utilized for detailed analysis and compared to results given by x-ray diffraction and thermal analysis. Deconvolution of the MAS spectra signals was based upon the Lorentz curve for best results and XRD quantification was performed by the Rietveld refinement method. Final strength testing was performed to obtain compression and tensile bending properties of the formed specimens.

The slag material (S) was determined to be 73 percent glass (by mass), crystalline calcium silicate phases and calcite. The metakaolin material (M) was found to be 84 percent

amorphous dehydroxylated kaolinite. Activation was achieved using a sodium hydroxide solution in specific proportion as to obtain equivalent Na/Al ratios (0.4) between both the pure metakaolin and pure slag binders. Molds were poured and cured at 40 °C for 24 hours. Bending strength test specimens were prepared as 1 x 1 x 6 cm prisms and the samples for the compressive strength tests were obtained from the resulting halves broken during bending and were cut to provide a 1 x 2 cm compressive area.

Compressive strength testing results showed a maximum value for the pure slag binder (AA-S) and an opposite value set for the specimens created from pure metokaolin (AA-M). The mixed designs (AA-M50/S50 and AA-M25/S75) yielded similar results to the AA-S product. Similar trends were reported for the bend testing regimes for all samples.

XRD analysis revealed mainly amorphous phases for all pastes, but fresh crystal formation was only observed in samples containing slag material. Evaluation of the AA-S sample identified C-S-H phase crystals in small quantities. The thermal analysis routine subjected all specimens to temperatures ranging from 30 °C to 1000 °C at a rate of 10 K/min and measured the mass loss of water within the system. The ^{29}Si NMR routine reported results similar to initial expectations: the AA-M formed ASN with Q_4 signals, while the AA-S material formed C-S-H phases bearing Q_1 and Q_2 signals. The ^{27}Al NMR spectra illustrated four coordinated aluminum for both AA-M and AA-S, yet the AA-S specimen additional revealed hydrotalcite seen as six-coordinated aluminum. This was confirmed via x-ray diffraction. Regardless, the overall reaction degree of the slag material was much greater than that mixed with metakaolin.

In conclusion, it was stated that the minute interacted witnessed between the two products was due to variable dissolution kinetics and was related to the aluminum transfer into the C-S-H phase, resulting in a reduction of the Si/Al ratio from 6 to 2.8 and a C-S-H chain length increase from 6 to 13. The metakaolin/slag mixes were seen to yield both calcium silicate hydrates and polymer product blends, thus working together to increase mechanics. The establishment of independent reaction degree within the blended mix was not achieved. It was stated that additional tests (including ^{1}H-^{27}Al CP NMR and MQ^{27}Al NMR techniques) will be performed to obtain a deeper understanding of the reaction products formed and the quantification that exists within the metakaolin/slag blends.

Puertas, F., Martinez-Ramirez, S., Alonso, S., Vazquez, T., "Alkali-Activated Fly Ash/Slag Cement : Strength Behavior and Hydration Products", *Cement and Concrete Research 30***, pp. 1625-1632, 2000.**
The research conducted for this paper focuses upon alkali-activation for various ratios of fly ash/slag mixtures and the resulting mechanics achieved relative to each specimen series. The molar concentrations of sodium hydroxide (NaOH) used were 2/10 M and the fly ash/slag ratios were as follows: 100/0, 70/30, 50/50, 30/70, 0/100. Mixed pastes were cured at 25 °C and 65 °C for comparison and resulting reaction products were analyzed using HCL dissolution techniques to obtain reaction degree, XRD, FTIR, and MAS-NMR analysis methods.

The pozzolanic materials obtained were Spanish fly ash of mainly glass consistency and a commercial blast furnace slag with high amounts of CaO and SiO_2 present. The materials were mixed separately in the proportions stated above and activated with the applicable alkaline concentration to form the paste of liquid/solid ratio of 0.35. Fresh samples were

formed into prismatic molds (1 x 1 x 6 cm) and allowed to cure for five hours in 98 percent relative humidity; one series at 25 °C and the other at 65 °C.

Compressive strength testing commenced at 1, 7, 28 and 90 days of cure time and it was found that strength increased proportionally with slag content increase. In addition, the highest strengths recorded (almost 70 MPa at 90 days, 0/100 fly ash/slag ratio) were observed from the specimens with the highest alkaline concentration of 10 M. Of the three main factors evaluated in potential strength gain, activator concentration and fly ash/slag ratios were the most vital. Temperature gain was observed to have a direct affect on the dissolution of the pozzolans, resulting in a greater reaction degree and less porous, stronger matrix consisting of a tetrahedrally-formed hydrated calcium silicate gel. Thus, the low reactivity measured from specimens at ambient temperature was justified.

Insoluble residue (IR) of the 50/50 mix was measured at 37 percent through HCL dissolution of reacted slag and fly ash particles. It was noted that the IR was observed to decrease as the cure time of each specimen increased, which was concluded to be the affect of a continually decreasing amount of available ash/slag particles for potential reaction and subsequent HCL dissolution. In most cases, the slag would dissolve more easily than the fly ash material, therefore, little to no hydrated alkaline aluminosilictes resulting from fly ash activation was observed.

SiO$_2$/Na$_2$O RATION AFFECTS

Criado, M., Fernandez-Jimenez, A., Palomo, A., Alkali Activiation of Fly Ash: Effect of the SiO2/Na2O Ratio. Part 1: FTIR Study", *Microporous and Mesoporous Materials 106***, pp. 180-191, 2007.**

This paper analyzes alkali-activated fly ash cements at micro levels using infrared spectroscopy to identify bonding activity within the polycondensed gel formation. Special attention was paid to the initial silicate proportion in the activating solution and the reaction products formed with the class F fly ash material. All alkali-based solutions consisted of sodium hydroxide (NaOH) and various levels of soluble silica for comparison and were mixed with the fly ash material at a 0.4 (liquid/solid) ratio for all samples.

Specimens were cured at 85 °C and tested at 8 hours, 60 days and 180 days using an ATI Mattson Genesis spectrometer device in a range from 4000 to 400 cm^{-1} per the KBr pellet method. The original fly ash material was tested and found to contain quartz and mullite in a vitreous phase and the same in crystalline phase. Once immersed into solution, the activated ash precipitated zeolites and aluminosilicate gel. To more clearly define the nanostructure of the reacted ash, FTIR spectra was conducted as related to curing temperature and soluble silica in the initial ash and reported as T-O bond asymmetric stretching band spectra in the 996-1145 cm^{-1} range. As well, external ring vibrations of the silicate and aluminosilicate cyclic structures became apparent in the fly ash activated solutions as spectra in the 800-500 cm^{-1} range.

Criado, M., Fernandez-Jimenez, A., de la Torre, A.G., Aranda, M.A.G., Palomo, A., "An XRD Study of the Effect of the SiO$_2$/Na$_2$O Ratio on the Alkali Activation of Fly Ash", *Cement and Concrete Research 37***, pp. 671-679, 2007.**

This research paper discusses the affects of varying concentrations of soluble silica in fly ash-based cement pastes. Four different alkaline solutions were used in the activation design.

Subsequent mechanical testing and x-ray diffractometer analysis was conducted at various curing intervals. Additionally, a quantitative test was performed using hydrochloric acid (at a 1:20 ratio by volume) to dissolve reacted ash particles. The unreacted, insoluble residue was collected, calcined at 1000 °C for one hour and measured to determine the overall reaction degree (α).

A type F fly ash composed mainly of SiO_2 and Al_2O_3 was obtained from a steam power plant in Spain and used throughout the experiment for all paste specimens. Activation of the fly ash substance was completed using a sodium hydroxide alkali solution of varying soluble silica proportions. Testing comparisons between the different paste mixtures were observed and reported.

Prismatic molds (1 x 1 x 6 cm, 12 per test) were formed using a solution/ash ratio of 0.4 (by weight) and allowed to cure at 85 °C (greater than90 percent relative humidity) for the following time intervals prior to evaluation and testing: eight hours and 7, 28, 60, 90 and 180 days. It was found that an increase of soluble silica improved mechanical strength at shorter curing intervals. However, longer curing intervals revealed an increase in mechanical strength regardless of silica content. Compressive strength values of 70 MPa were recorded for all specimens at the 90 day interval and a strength of 90 MPa was observed in the W50 specimen.

XRD analysis illustrated a sharp decline in the vitreous phase with increasing reaction times for all specimens. It was concluded then that vitreous phase dissolution is the mechanism by which alkaline reactions occur. As the silica dissolves and becomes polymerized, reaction time slows. It was stated that the reaction degree is directly related to the aluminosilicate gel and zeolitic formation within the matrix and that zeolite formation occurs relative to gel percentages. For this reason, it was concluded that aluminosilicate gels are zeolite precursors. Thus, the highest mechanical strengths recorded were a product of high soluble silica concentrations.

Research conclusions were stated in terms of mechanical strength factors derived from the nature and composition of the initial alkaline activators in combination with the selected fly ash material. High levels of soluble silica in the activator system produce an increased percentage of sodium aluminosilicate gel, which in turn, nurture the formation of zeolite crystals and a condensed, cementitious material.

DRY SHRINKAGE

Krizan, D. and Komljenovic, M., "Mortar Based on Alkali Activated Blast Furnace Slag: Microcracks Formation as a Result of the Drying Shrinkage Process", *M.S. Konsta-Gdoutos, (ed.), Measuring, Monitoring and Modeling Concrete Properties*, **pp. 361-366, 2006.**
The research conducted for this paper focuses upon linear deformations of blast furnace slag-based cements activated with various SiO_2/Na_2O mass ratios (n modulus) of water glass. Water glass moduli and concentrations used for experimentation were (n=0.6, 0.9, 1.2, 1.5) and (3 percent to 4 percent Na_2O) with the slag specific surface area varying from 430 m^2/kg to 600 m^2/kg. Deformation measurements of the slag material were compared to that of ordinary Portland cement mortar.

The slag specimens were prepared with a water/slag ratio of 0.43 and the Portland samples were given a 0.5 water/cement ratio. A sand aggregate was incorporated at a 1:3 ratio

(binder/sand) prior to being molded into 40 x 40 x 160 mm bars for testing. Curing in the mold occurred over a 24 hour period in climate controlled conditions. The temperature was maintained at 20±2 °C with a relative humidity of 50±5 percent. Testing measurements (per standard JUS BC.8.029/79) commenced once the molds had been removed and continued intermittently over a 28 day period.

Test data revealed that linear deformation occurs relative to the water glass modulus and concentration, but regardless of specific surface area of the slag. The majority of deformation occurred within the first 21 days. It was stated that the deformation measured in the slag mortars were continuously higher than those observed in the Portland samples. While the main factor affecting linear deformation was found to be the water glass modulus and concentration, a negligible increase in deformation was stated to occur with increased specific area, but only in high water glass modulus and concentration environments.

The main reaction product of water glass activated slag mortars was found to be a poorly crystallized calcium silicate hydrate (C-S-H) formation. Rapid formation of this crystal was noticed and used to explain the high early strength values reported by others for mortars of this design. Close analysis of the hardened material revealed microcracks on the order of 10-20 μm in length. It was then concluded that while water glass activated slag mortars produce high compressive strength values due to the formation of C-S-H, the same formation bears negative influence through propagated cracking of the final matrix.

VARIABLE CURING METHODS

Kovalchuk, G., Fernandez-Jimenez, A., Palomo, A., "Alkali-Activated Fly Ash: Effect of Thermal Curing Conditions on Mechanical and Microstructural Development – Part II", *Fuel 86***, pp. 315-322, 2007.**

This research investigates the mechanical and microstructural affects upon alkali-activated fly ash cement due to various curing methodologies. Three separate routines are examined and tested: Covered Curing Mold (CCM) at 95 °C, Dry Curing at 150 °C, and Steam Curing at 95 °C. Several methods of testing and observation were employed including x-ray difffraction, FTIR spectroscopy, ^{29}Si MAS-NMR, mechanical strength, water content and pore structure analysis.

Class F fly ash with a Blaine Fineness of 202 m^2/kg was mixed with soluble sodium silicate (3.35 modulus) and water at a ratio of 0.18 (water/solid). The resulting binder agent was molded and immediately covered with plastic to eliminate possible evaporation of the samples. Curing of the specimens followed per the methodologies listed above. CCM samples were placed in a heated oven environment at 95 °C for 8 hours prior to analysis. DC samples were treated differently in that they received a two hour cure at 95 °C and were then allowed to cool to ambient before being ramped back to 150 °C within three hours and back to ambient in another three. This method of curing was stated to be a common practice in the industry for precast concrete. Finally, the SC samples underwent a similar scenario with the following exceptions: two hours at 95 °C, cool to ambient, ramp to 95 °C in three hours and held for six hours, then back to ambient in another three hours. It was noted that the relative humidity was constant among all test regimes.

Compressive testing revealed that curing under CCM condition produced the highest strength results of up to 102 MPa. Increases of soluble silica and alkali content boosted the values, as

well. The lowest recorded strength value was yielded by the DC specimens and was stated to be a direct result of rapid water loss during cure. The SC specimens saw an optimum strength from mixes with a SiO_2/Al_2O_3 ratio and fell between the CCM and DC methods for overall mechanical strength.

X-ray diffraction analysis proved that the reaction compound from fly ash activation is mainly an amorphous compound with traces of crystalline structures present. Hydroxysodalites, herschelites and thermonatrites were also found in small amounts; the existence of thermonatrites was stated to indicate possible carbonation occurring in the matrix which would result in a decrease in fly ash activation and a subsequent loss of strength. However, the trace amounts identified were stated to be of no consequence to mechanical performance of any of the specimens tested.

Further ^{29}Si MAS-NMR analysis found formations of aluminum-rich tectosilicates heavy with Q^4(4Al) units (-88ppm) in all curing samples and their predominance was categorized from greatest to least abundant as follows: dry curing greater than steam curing greater than CCM. Since mechanical performance is enhanced with increased Si content in the aluminosilicate gel, these formations rich in aluminum are likely to be less resistant to compressive forces. This follows the compressive strength data results which reported the dry cured samples as being least in mechanical strength.

It was concluded that water is the essential ingredient to fly ash reactivity and high levels of humidity are required during cure time to reduce negative carbonation effects and to achieve satisfactory cement properties. An increased reaction percentage is stated to yield an increased matrix density and a decreased overall porosity, thus improving structure and increasing mechanical strength. This agrees with the CCM mold results which stated they were found to be very dense and of high strength; lack of evaporation allowed greater reactivity of the ash. The dry cured molds allowed for full evaporation of internal water and inhibited fly ash reaction potential. Therefore, it is recommended to use dry-curing only for binder mixes utilizing an NaOH activator, since the presence of waterglass will slow reaction kinetics.

ULTRASOUND TREATMENT AFFECTS

Feng, D., Tan H., and Van Deventer J.S.J., "Ultrasound Enhanced Geopolymerisation", *Journal of Materials Science 39***, pp. 571-580, 2004.**

This research investigates the possibility of increasing the compressive strength of metokaolinite/fly ash and metokaolinite/sand-based geopolymer cements using ultrasonication. The theory for experimentation was that the ultrasonic waves may aid to condense the paste medium and allow for increase reaction degrees within the matrix. Analytical evaluations were performed using SEM analysis, XRD and ^{27}Al and ^{29}Si MAS-NMR technologies. It was stated that the SEM analysis was the key to unveiling microstructure of fractured surfaces and the elemental content of the gel phase. Metokaolinite and fly ash materials were obtained and chemical contents reported for each. Fine washed beach sand was employed as an aggregate filler in all metakaolinite mixes and sodium silicate and potassium silicate solutions were utilized for alkaline activation.

Prior to geopolymerization of each pozzolanic substance, an initial leaching experiment was conducted using both NaOH and KOH and a leaching solution to identify and characterize

elemental content of Al, Fe, Ca, and Si within the samples. Ultrasonication was employed with a power intensity of 300 W/cm^2 to enhance dissolution and subsequent samples were tested and quantified at given time intervals using a concentrated HCl solution for neutralization. Additional dry samples were used for actual geopolymerization and activated with a chosen alkaline solution (KOH and/or NaOH). Ice water was used to retard hardening while ultrasonication was performed in the slurry. As a control, a vibratory shaking device was also used on another sample set to provide comparison results against specimens receiving ultrasonic treatment. Both slurries were molded in PVC cylinders of dimension (28 x 55) mm and cured at 40 °C for 24 hours, prior to being de-molded and stored at 20 °C for ten additional days. Upon reaching full cure term, specimens were tested for compressive strength and the calculated average strength measurements were recorded.

It was reported that final compressive strengths of the tested specimens increased as a result of the ultrasonic application. It was believed that the ultrasonic treatment of the initial slurry aided in increased Si/Al dissolution, thus providing increased gel formation for polycondensation. This theory was supported through SEM analysis of the hardened matrix as heterogeneous distribution of the gel phase was observed. XRD evaluation revealed enhanced crystalline formations throughout the specimen matrices. ^{27}Al MAS-NMR spectra showed chemical shifts at -55 ppm, suggesting a presence of tetrahedrally-coordinated aluminum of form Al(4Si). Thermal resistance of the hardened cement was also found to have increased due to the ultrasonic process. This was attributed to accelerated Si-Al dissolution and subsequent increases in the degree of alkaline reaction. It was concluded that ultrasonication improves the overall mechanical properties of metakaolinite/fly ash based, alkaline activated cementitious materials.

HAZARDOUS WASTE CONTAINMENT

Luna, Y., Querol, X., Antenucci, D., Jdid, El-Aid, Fernandez-Pereira, C., Vale, J., "Immobilization of a Metallurgical Waste Using Fly Ash-Based Geopolymers", *2007 World of Coal Ash, Covington, Kentucky, USA***, May 7-10, 2007.**

The report investigates the use of class F fly ash-based geopolymer cements as tools to encapsulate electric arc furnace (EAF) dust and minimize potential leaching of hazardous metals (Pb, Cd, Cr, Zn) into surrounding systems. Additional lime, silicon and silicoaluminate substances were used as secondary agents including blast furnace slag, kaolinite and local clays. Experimentation was conducted from the perspective of curing conditions, alkaline activators and respective concentrations, resulting compressive strength values and chemical resistance. Leaching tests were performed to define and understand its potential to stabilize and solidify heavy metal waste products for commercial use. Sodium hydroxide, potassium hydroxide and sodium silicate were all tested as suitable alkali-activators for the pozzolanic material and a series of Portland cement mixes were utilized for direct comparison to the geopolymer data. All experimentation was performed per EPA and EULFD regulations.

The fly ash material was obtained from a coal power plant in Spain and was mix proportionately with either a NaOH or KOH solution and a silicoaluminate to produce the geopolymer paste. Cylindrical molds were formed and compacted prior to cure at both room temperature and 60 °C, depending upon the test regime. Compressive strength tests were then conducted at time intervals of 7, 14, and 28 days.

The ash material was again used for mixing with the EFA dust to create S/S solids. Formed pastes were transferred to cylindrical molds measuring (30 mm diameter x 41 mm height) and compacted and vibrated to remove trapped air improve density within the matrix. As with the fly ash samples, the S/S specimens were subjected to curing of two types: ambient and 60 °C elevated temperatures. All samples were bagged to prevent moisture escape during cure and after seven and 28 days, specific specimens were removed from mold, crushed, sieved and extracted by leaching techniques. The others were utilized in compressive strength analysis.

Testing showed that longer curing times and higher temperatures produce stronger cement samples for most specimens. However, those incorporated with kaolinite and metakaolinite actually produced an inverse affect: structural stability weakens with increased temperature. Compressive strengths of 25 MPa were obtained from samples containing KOH and cured at 60 °C, while the lowest values recorded were from the same mix cured at ambient temperatures. Nevertheless, it was noted that samples containing potassium hydroxide as an activator produced stronger samples than those using sodium hydroxide. Therefore, it was determined that potassium content plays a direct role in compressive strength of geopolymer cements.

Finally, leaching tests revealed that S/S solids containing KOH encapsulated heavy metals better than all others tested. The PCC samples leached large amounts of Zn, Pb and Cr and were not recommended for use in hazardous waste containment, but samples performing the worst relative to leaching were those created using kaolinite material. While these samples underperformed others tested, all experimental specimens (with the exception of PCC) remained within the limits set forth by the regulation guidelines and could therefore be considered for use in commercial containment products.

LIST OF SYMBOLS, ABBREVIATIONS, AND ACRONYMS

AAS	alkali-activated slag
ADR	airfield damage repair
AFRL	Air Force Research Laboratory
Al_2O_3	aluminum oxide
$Al_2Si_2O_5(OH)_4$	kaolin, kaolinite
AOS	Aircraft Operating Surfaces
ASR	aluminosilicate reactivity
$Ca_2MgSi_2O_7$	Åkermanite, a mineral containing calcium, magnesium, silicon, and oxygen
CaO	calcium oxide
Cd	cadmium
cm	centimeter(s)
cm^2/g	square centimeter per gram
CO_2	carbon dioxide
Cr	chromium
C-S-H	calcium silicate hydrate
EHE	Spanish Structural Concrete Code (EHE in Spanish)
Fe_2O_3	iron oxide
FTIR	Fourier Transform Infrared Spectrometry
g	gram(s)
GGBFS	ground granulated blast furnace slag
H_2SO_4	sulfuric acid
HCl	hydrochloric acid
ITZ	interfacial transition zone
K_2CO_3	potassium carbonate
K_2SO_4	potassium sulfate
KOH	potassium hydroxide
MAS-NMR	Magic Angle Spinning-Nuclear Magnetic Resonance
MgO	magnesium oxide
$MgSO_4$	magnesium sulfate
mm	millimeter(s)
MPa	mega pascal, unit of pressure
N/mm	Newton per millimeter
NaOH	sodium hydroxide
$NaAlSiO_4$	nepheline, mineral containing sodium, aluminum, silicon, and oxygen
Na_2CO_3	sodium carbonate
Na_2O	sodium oxide
Na_2SiO_3	waterglass; sodium silicate
Na_2SO_3	sodium silicate
Na_2SO_4	sodium sulfate
nm	nanometer
NO_x	nitrogen oxides
$nSiO_2K_2O$	potassium waterglass
$nSiO_2Na_2O$	sodium waterglass
Pb	lead

PCC	Portland cement concrete
psi	pounds per square inch
PVA	polyvinyl alcohol
SEM	Scanning Electron Microscopy
Si-O-Al	silicon-oxygen-aluminum
SiO_2	silicon dioxide
SSD	saturated surface dry
XRD	X-ray Diffractometer
Zn	zinc
°C	degrees Celsius
°F	degrees Fahrenheit
μm	micrometer, 0.001mm